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O. J. FLECKER

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BY

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PREFACE

THIS book was written from a desire to put into practice certain aspects of teaching Chemistry which were emphasized at the Board of Education Vacation Course in Chemistry held at Oxford in 1921.

Stress is laid from the beginning on the principles of Physical Chemistry, and although at first sight it may appear inappropriate or impracticable to introduce beginners to the Ionic Theory or Reversible Reactions, yet the experience of the last two years has convinced the author of the value of this procedure, even if judged from the standpoint of examination successes.

Mr. D. Ll. Hammick, Fellow of Oriel College, read through the manuscript, and to him the author is indebted for many valuable suggestions and for kind permission to include several experiments which he devised.

The author is also indebted to a number of text-books of Inorganic Chemistry, in particular to Alexander Smith's *Introduction to Inorganic Chemistry*, and to Miss Freund's *Experimental Basis of Chemistry*.

O. J. FLECKER.

DEAN CLOSE SCHOOL, CHELTENHAM.
October, 1923.

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CONTENTS

CHAPS. PAGE

I. Solution 1

II. Crystals 11

III. Chemical Change and the Conservation of Mass 16

IV. Elements, Compounds, and Mixtures . . 19

V. Hydrogen and Water 23

VI. Oxygen and Water. The Properties of Gases 30

VII. Nitrogen and Air 38

VIII. Oxides 45

IX. Carbon Dioxide 52

X. Carbonates and Bicarbonates . . . 63

XI. Hard and Soft Waters 68

XII. Some reactions of Acids, Bases, and Salts . 73

XIII. Equivalent Weights 78

XIV. The Law of Multiple Proportions: Atomic Theory 86

XV. Chlorine 89

XVI. Hydrochloric Acid and Equations . . . 94

XVII. The Chlorides: Valency 101

XVIII. Acids, Bases, and Salts: Electrolysis . . 107

XIX. A Formula for Water: Fixing Atomic Weights 114

XX. Oxygen (Revision); Peroxides; Oxidation and Reduction; Hydrogen (Revision) . . 118

XXI. Sulphur and Sulphuretted Hydrogen , . 126

CHAPS. PAGE

XXII. Sulphur Dioxide, Sulphur Trioxide, Sulphuric Acid 134

XXIII. Acidimetry and Alkalimetry . . . 144

XXIV. Nitrogen and Ammonia 150

XXV. Nitric Acid and the Oxides of Nitrogen . 161

XXVI. Carbon, Coal-gas, Carbon Monoxide, Hydrocarbons 174

XXVII. Flame: The Blowpipe 184

XXVIII. Phosphorus: Chemical Families . . 190

XXIX. Silica: Glass: Finding a formula from a given percentage composition . . . 197

XXX. Metals and Non-Metals. Sodium and its principal compounds. Comparison with Potassium and Ammonium . . . 200

XXXI. Calcium. Magnesium. Zinc . . . 210

XXXII. Copper. Lead. Iron 218

INDEX 235

I

SOLUTION

EXPERIMENT 1.

To find out whether salt loses weight when dissolved in water.

Weigh a beaker containing about 50 c.c. of water and covered by a watch-glass on which are a few grams of salt. Empty the salt into the water, avoiding loss by spilling or splashing, replace the watch-glass and weigh again. Tabulate your results thus:

Weight of beaker + watch-glass + salt (undissolved) = gm.
Weight of beaker + watch-glass + salt (dissolved) = gm.

From your results write your conclusion.

Note that it clearly does not matter if all the salt is not transferred to the beaker after the first weighing, provided that what is left is weighed on the watch-glass in the second weighing and not spilled.

EXPERIMENT 2.

To recover a dissolved solid by evaporation.

Pour some sodium carbonate (washing-soda) solution into an evaporating dish, place the dish on a wire-gauze supported on a tripod, and heat gently to avoid loss by spirting. When the liquid has been driven off as vapour (evaporated) the remaining solid is sodium carbonate.

Find out if there is any dissolved solid in (*a*) tap-water, (*b*) distilled water, by holding a drop of the water on a piece of broken glass a few inches above a Bunsen flame and evaporating to dryness.

EXPERIMENT 3.

To find if there is a limit to the amount of a solid which can be dissolved in a given quantity of liquid.

Place 50 c.c. of water at about room temperature in a beaker and weigh. Add very small quantities of finely powdered copper sulphate (blue vitriol), each time stirring until the solid has all dissolved before any more is added.

Note: Do not poke the stirring-rod through the bottom of the beaker. The best way to avoid doing this is to keep the end of the rod always on the bottom of the beaker.

After a time you will find that no more will dissolve. Find the temperature of the solution with a thermometer, and weigh the beaker and its contents. Tabulate as follows:

Weight of beaker + solution at first temp. = gm.
Weight of beaker + water = gm.
∴ Weight of solid dissolved at first temp. = gm.

This weighing will give you a very rough idea of how much copper sulphate will dissolve in 50 c.c. of water at the room temperature.

Now heat the solution up to 80° C., remove the burner, and continue the addition of the solid as before until a limit is again reached. Again find the temperature (now well below 80° C.) and weigh.

Make a table of weights similar to the one above to show the weight of solid dissolved at the higher temperature.

The conclusion to be drawn from this experiment is that there *is* a limit to the amount of a solid which can be dissolved by a given quantity of liquid, but that this limit varies as the temperature is changed. The experiment must not be taken as giving at all an accurate result for the amount of copper sulphate dissolved in 50 c.c. of water at the two temperatures. The two main sources of error are:

(1) That an excess of solid beyond what is dissolved is weighed in both cases.

(2) That during the heating up to 80° C. some of the water will evaporate, so that in the second experiment there is not so much as 50 c.c. of water in the beaker.

A more accurate way of finding the amount of solid that will dissolve in a given quantity of liquid at a given temperature is given in Experiment 5.

EXPERIMENT 4.

To make a solubility curve for potassium chlorate.

Into a number of test-tubes, each fitted with a thermometer passing through a loosely bored cork, place weighed quantities of finely powdered potassium chlorate. Suitable quantities are 0·75, 1, 1·25, ... up to 3 or 4 grams. Each member of the class should choose a different weight, and the final result is obtained from the work of all the different members. Add 10 c.c. of distilled water from a pipette to each test-tube, and warm each tube in a beaker of water until all the solid has dissolved. Allow the liquid in the test-tube to cool, keeping it stirred with the thermometer, and note carefully the temperature at which crystals reappear. The class results are tabulated as follows:

Weight of potassium chlorate.		Crystallizing temperature.
(*a*) in 10 c.c. water	(*b*) in 100 c.c. water	

The readings in the last two columns are then plotted on squared paper.

When a given quantity of liquid has dissolved as much of a given solid as possible at a given temperature it is said to be saturated with that solid. In this experiment the temperatures are recorded each time just as the solid reappears: that is, just as the liquid becomes saturated with the amount of solid in it.

The number of grams of a given solid required to saturate 100 grams of a liquid at a given temperature is called the solubility of that solid in that liquid at that temperature. Since 100 c.c. of water weigh 100 gm., the second column of the table gives the solubilities of potassium chlorate in water at the temperatures shown in the third column. It is thus clear that we can read off from the graph the solubility of potassium chlorate at any temperature within the limits of the experiments made. Such a graph is called a solubility curve.

EXPERIMENT 5.

To find the solubility of potassium nitrate at the temperature of the room.

Note : The solution for this experiment should be prepared at the lesson before the one in which it will be used.

Finely powder about 15 gm. of potassium nitrate (nitre) and place in a bottle with 50 c.c. distilled water. Shake well and leave to stand so that the solution may become saturated.

Caution : When you are ready to start the experiment do not shake up the excess of solid into the clear solution nor stir it up with the pipette.

Weigh an evaporating dish, note the temperature of the solution, suck up some of it (the volume does not matter) and place in the dish. Weigh the dish and solution. We now require to find the weight of potassium nitrate in the known weight of solution, and to do this we must evaporate off all the water, or, as we say, evaporate to dryness. This process must be carried out slowly so that there is no loss of the solution by spirting. If a hot-plate is available that can be used, and, if not, the evaporating dish may be placed on a spouted beaker in which water is boiled, as in this way the temperature of the solution will not rise above 100° C., the boiling-point of water. The steam from the beaker escapes through the spout. An arrangement of this kind is called a water-bath. In order to make sure that the potassium nitrate has been completely dried, it should be alternately heated, cooled, and weighed until the weight is constant. (Wipe the underneath of the beaker before weighing.)

Evaporate to dryness on a hot-plate or water-bath. Weigh the dish and residue (i. e. what is left). Tabulate your results as follows:

Weight of dish + solution = gm.
Weight of dish empty = gm.
Weight of solution = gm.

Weight of dish + residue = gm.
Weight of dish empty = gm.
Weight of residue = gm.

Weight of solution = gm.
Weight of residue = gm.
Weight of water = gm.

From your results calculate what weight of potassium nitrate would be dissolved by 100 gm. of water at the temperature of your experiment. This is the solubility of potassium nitrate at this temperature.

EXPERIMENT 6.

To find out if calcium sulphate is soluble in water.

Shake up some calcium sulphate in distilled water in a test-tube; none appears to dissolve. Warm the water nearly to boiling-point and filter the liquid. A drop of the filtrate (liquid which passes through the filter) evaporated on a piece of glass, as explained in Experiment 2, will leave a considerable residue, showing that the solid is not totally insoluble.

Calcium sulphate is found in most soils, and therefore water flowing through these soils is likely to contain some dissolved calcium sulphate.

EXPERIMENT 7.

Separation of a soluble from an insoluble substance :

(a) sulphur and iron filings,

(b) sand and salt.

(*a*) Neither sulphur nor iron is soluble in water, but sulphur is soluble in a liquid called carbon disulphide. This is a very volatile liquid (i. e. it turns to a gas at a very low temperature, 46° C.) and its vapour is highly inflammable. All burners must therefore be put out before starting this experiment. Shake up one or two grams of the mixture in half a test-tube of carbon disulphide. Filter into a crystallizing dish and set aside. If all the dishes are placed in a fume cupboard the burners can safely be lit for the next experiment. After a short time crystals of sulphur will appear in the dishes. The iron is left on the filter.

(*b*) Weigh a beaker, place in it 5–10 gm. of the mixture and weigh again. Add about 80 c.c. of water and boil for some minutes. Weigh a filter paper and filter the solution. Carefully wash all the sand into the filter with the wash-bottle. Wash the sand on the filter two or three times with small quantities of hot water to ensure the removal of all the salt. Throw away all the filtrate.

Put the funnel containing the filter into a hot oven to dry. When quite dry remove the cone containing the sand and weigh. Tabulate your results as shown, and calculate the percentage composition of the mixture (i. e. the weights of sand and salt in 100 gm. of the mixture):

Weight of beaker + mixture = gm.
Weight of beaker empty = gm.
Weight of mixture = gm.

Weight of filter paper + sand = gm.
Weight of filter paper = gm.
Weight of sand = gm.

Nobody has found out how it is that a liquid has the power of dissolving certain solids, but something is known of the internal structure of liquids and solids which helps us to understand what is taking place when a solid dissolves.

If we had a means of seeing things very much smaller than the most powerful microscope can show us, we should find every solid made up of minute particles called molecules which cohere (i. e. stick together) more or less closely. Liquids are also made up of molecules, but these molecules are farther apart than is the case with solids, and they move about, and do not have much cohesion. This explains why liquids tend to spread out over any surface on which they are poured, while solids keep their shape. It also leads us to expect that there would be a class of substances on the border-line between liquids and solids. This we find to be the case, the very viscous liquid pitch, which cannot be poured from one vessel to another on account of its strong cohesion, being an example.

In gases the molecules are still farther apart and move faster than is the case with liquids. Thus we see that when we heat a solid and cause it to melt or fuse, and then continue the heating and turn the liquid into a gas, what we are doing is to give the heat-energy of the flame to the molecules and thereby increase their speeds. The molecules are also driven farther apart, because, having more energy, they hit each other harder, and bounce farther apart, and the result of this is seen in the expansion of solids, liquids, and gases on heating.

The evaporation of liquids is also explained by this theory. If we suppose the molecules of a liquid to be in motion it is clear that those which are at the surface of the liquid will tend to move away from the main body of the liquid from time to time, and if while they are doing this they are wafted a little farther by a current of air they will get beyond the region of the attractive forces of the molecules left in the liquid, and will therefore not return to it. Thus to cause rapid evaporation we must have:

(*a*) a large surface so that as many molecules as possible shall be in the surface layer;
(*b*) a good draught to waft the molecules away;
(*c*) heat to make the molecules move as fast and as far away from each other as possible.

When a solid is placed in a liquid, the liquid molecules bombard the solid ones and are often able to drive them so far apart from each other that the shape of the solid is lost: in other words the solid dissolves. The dissolving liquid is called the solvent and the dissolved solid the solute. The solution of a solid in a liquid whereby the molecules of the solid are torn apart by those of the liquid should be carefully distinguished from the fusion of a solid where heat-energy is the cause of the tearing apart of the solid molecules. Both solution and fusion (melting), however, mean a change from the solid to the liquid state, and we might therefore expect that since a certain amount of heat, called the latent heat, is absorbed when a solid is melted, heat might also be absorbed when a solid is dissolved. If you take the temperature of a test-tube of water and then add to it some ammonium nitrate, you will notice a very considerable fall of temperature: i. e. heat is being absorbed as the ammonium nitrate dissolves. Most solids show a fall of temperature on solution: but in some cases there is a rise of temperature, which is always due to some action (beyond ordinary solution) taking place between the solid and the water. (See next chapter.)

EXAMPLES ON CHAPTER I.

1 The following table shows the solubilities of ammonium chloride in water between 0° C. and 100° C.:

Temp.	0°	10°	15°	20°	40°	60°	80°	100°
Sol.	29·4	33·3	35·2	37·2	45·8	55·2	65·6	77·3

Draw the solubility curve for ammonium chloride and read off the weight of this substance which will dissolve in 100 gm. of water at 47° C.

2 Calculate the solubility of potassium nitrate in water at 15° C. from the following data:

Weight of dish + solution = 43·75 gm.
Weight of dish + residue = 18·40 gm.
Weight of dish empty = 12·25 gm.

3 5·65 gm. of a mixture of iron and copper contain 3·29 gm. of iron. What is the percentage composition of the mixture?

II

CRYSTALS

EXPERIMENT 8.

To prepare crystals of copper sulphate and to observe the effect of heat on these crystals.

Make a hot saturated solution of finely powdered copper sulphate, pour it into a crystallizing dish, and set aside. Proceed with Experiment 9 until crystals have formed. Dry some of the crystals by pressing between filter paper, and heat them in a test-tube with the mouth held lower than the closed end. Note the moisture given off and the change of colour from blue to a greyish-white. Shake the powder on to a watch-glass and add a few drops of water. Note the return of the blue colour.

Experiment 9.

To find the percentage loss of weight when sodium carbonate is heated.

Finely powder some crystalline sodium carbonate and weigh out accurately into a weighed crucible as much as will half fill it. Heat on a triangle with very small flame and the lid closed at first; when there is no further spluttering, the lid should be raised and the size of the flame increased until the bottom of the crucible is red-hot. Allow to cool and weigh. This important process of alternate heating and weighing, which we used in Experiment 5, is continued until there is no further loss of weight.

Tabulate as follows:

Weight of crucible + sodium carbonate = gm.
Weight of crucible empty = gm.
Weight of sodium carbonate = gm.

Weight of crucible + contents after first heating = gm.
Weight of crucible + contents after second heating = gm.

(This is repeated as often as necessary; the number of heatings should always be able to be seen clearly from the table of weights.)

The first weight on the table minus the last weight of all is the loss of weight of the particular weight of sodium carbonate you used. You can therefore now find by proportion what is the loss in weight of 100 gm. of sodium carbonate crystals when heated until its weight is constant.

EXPERIMENT 10.

To find out what happens when ammonium chloride is heated in a test-tube.

Heat about a gram of pure ammonium chloride crystals in a clean dry test-tube. Make a record of all that you observe. (Heat the bottom of the test-tube only; do not heat the sides.)

Crystals are usually formed by cooling a strong solution below the temperature at which it is saturated (Experiment 4). Experience shows us that rapid cooling produces small crystals, and slow cooling large ones. We often notice other ways in which crystals are formed. If you look at a bottle in which camphor has been kept for some time you will probably notice tiny crystals formed near the neck. These crystals have been formed by *sublimation*, that is to say by the changing of a solid to a gas and from the gas back to the solid again without passing through a liquid state. This is what happens in Experiment 10 when you heat ammonium chloride. It is converted into a gas by the heat, and when this gas touches the cool part of the tube it turns back again to a solid.

Solid substances are frequently purified by crystallization from water (or other solvents such as alcohol, carbon bisulphide, &c.). Impurities which were present in the original solid are often left behind in the liquid when the new crystals form. This method of purification is called *recrystallization*. The smaller crystals will be purer than the larger ones, which are likely to contain small drops of solvent inside them. Some solids may also be purified by sublimation either by heating in a tube, or in an evaporating dish under an inverted funnel. The sublimed solid (called the sublimate) collects in the funnel and is scraped out as required.

Crystals are also sometimes formed when a melted solid, such as sulphur, is allowed to cool. Since crystals are formed both by evaporating a solution and by cooling a molten solid, we have another point of resemblance between solution and melting.

If a crystalline substance is hammered it will be found to break very easily and smoothly along certain definite directions. The fragments have highly polished plane surfaces. This property of crystals is spoken of as cleavage. Common salt cleaves into tiny cubes, and we can imagine the tiny cubes building up the large cubical crystals. In cases where the cleavage is not so simple it is not so easy to see how the big crystals may be built up from the small ones. By means of X-rays the internal structure of many crystals has been studied, and we know now that the difference between crystalline and non-crystalline substances is that the crystalline ones have a regular and definite internal structure; all the tiny particles are arranged according to a fixed plan, and it is this internal regularity which gives to the crystals their external regularity of shape and other interesting properties which we cannot consider here. When solids have no regular internal arrangement of particles they are non-crystalline, or, as we often say, 'amorphous'. This word means 'having no shape'.

The particles in a crystal may be all of the same kind, but often they are of different kinds. Water particles are often found as part of the crystal structure, and this water is then called water of crystallization. If this water is driven out by heat, the crystal structure will of course fall to pieces, as we found with copper sulphate (Experiment 8). The solid after the water has been driven out is said to be 'anhydrous' (without water); when it contains water of crystallization it is called a 'hydrate'. The rise of temperature observed when some solids are dissolved in water is due to the formation of hydrates. Just as grey anhydrous copper sulphate will pick up its water of crystallization again and go back to the blue form, so most substances which have been dehydrated (i. e.

have had water driven off) will readily take up that water again. Anhydrous calcium chloride, for example, is extensively used to remove water from gases, its action being due to its tendency to form a hydrate. Anhydrous copper sulphate can be used to show if water is present in a liquid like alcohol. The alcohol is shaken up with a little anhydrous copper sulphate, and if this turns blue we know there must have been water in the alcohol.

Some anhydrous substances have crystalline forms of their own: for instance, anhydrous copper sulphate can be crystallized out from strong sulphuric acid.

EXAMPLES ON CHAPTER II.

1 2·758 gm. of a crystalline substance gave off 1·076 gm. of water on heating. What was the percentage of water in the crystals?

2 The percentage loss of weight when crystalline sodium carbonate is heated is 62·9. Which will be the better value: anhydrous sodium carbonate at 9*d.* per lb., or crystalline sodium carbonate at 4½*d.* per lb.?

NOTES.

1 You should make a point of remembering the appearance and any other properties you have discovered of all the chemical substances you use. Those you have used up to the present are:

Salt, properly called sodium chloride.
Washing soda, properly called sodium carbonate.
Blue vitriol, properly called copper sulphate.
Nitre or saltpetre, properly called potassium nitrate.
Sal ammoniac, properly called ammonium chloride.
Ammonium nitrate.
Potassium chlorate.
Calcium sulphate.
Sulphur.
Iron.
Carbon disulphide.

2 There are many interesting and beautiful things to be found out about crystals. If you can use a microscope you can watch the crystals growing. You could also find out something about how the X-rays are used to examine the internal structure of crystals. If you feel interested in this sort of thing, ask your Chemistry master for advice on what to do and what to read.

III

CHEMICAL CHANGE AND THE CONSERVATION OF MASS

Experiment 11.

To compare the solution of zinc in hydrochloric acid with the solution of salt in water.

Place a few pieces of zinc in a test-tube and add dilute hydrochloric acid. Note that an inflammable gas is given off. When solution is complete try to recover the zinc by evaporation. Now make a solution of salt in water, notice that no gas is given off; try to recover the salt by evaporation.

Experiment 12.

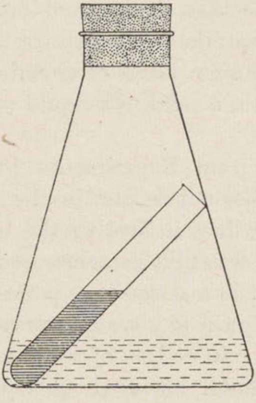
To compare the effect of heat on platinum and magnesium.

Hold a piece of platinum wire or foil in the flame for a few moments. Do the same with a piece of magnesium ribbon held in the tongs. Note what happens in each case.

EXPERIMENTS 13 (*a*) and (*b*).

To find out if a chemical change which occurs in a closed space is accompanied by any change in weight.

(*a*) **Into a conical flask pour 40 c.c. of lead nitrate solution and put 15 c.c. of potassium iodide solution in a small tube. Place the tube inside the flask as shown in the figure. Cork the flask firmly and weigh. Tilt the contents of the tube into the flask, note what happens, and weigh again. Write a conclusion from your result.**



(*b*) **Demonstration.**

A piece of phosphorus is placed on sand in a round-bottomed flask which is then tightly closed and weighed. The flask is gently warmed until the phosphorus starts to burn, and then covered with a large duster. When the action has ceased and the flask has cooled it is weighed again.

Experiments 11 and 12 illustrate the differences between what are called chemical and physical changes. A chemical change results in the production of a new kind of matter with a new set of properties. Thus zinc and the substance obtained by dissolving it in acid have different properties: but the salt is the same before and after it has been dissolved. Again, the heated magnesium is completely changed by burning, but the heated platinum is unchanged. The zinc and the magnesium have been permanently changed: we cannot at will reverse the process to turn them back into what they were originally, and we therefore say they have been through a chemical change. In the case of the salt and the platinum we noticed a temporary change: the salt disappeared from sight, and the platinum glowed brightly: but we can reverse this change and cause it to take place as many times as we like in either direction. Burning and rusting are two common forms of chemical change, and the change of state from a solid to a liquid or gas is a common physical change.

We also learn from Experiments 13 (*a*) and (*b*) that a chemical change does not consist in the creation of matter out of nothing, nor does it involve the total destruction of matter. This fact was first demonstrated by a great French chemist, Lavoisier, in a series of experiments, one of which consisted in heating tin in a sealed retort and showing that there was no total gain or loss of weight. He realized that this was a fundamental law of chemistry, and was the first chemist to put it into words or, as we say, 'formulate' it, although the fact had been generally assumed from the earliest times. This law is now usually spoken of as the Law of the Conservation of Mass, and may be stated thus: Matter cannot be created or destroyed.

IV

ELEMENTS, COMPOUNDS, AND MIXTURES

EXPERIMENT 14.

Mix together as well as possible some powdered sulphur with about half its bulk of iron filings.* Heat some of the mixture in a test-tube. After a short time a bright glow starts at one point, and then the glow (incandescence) travels through the whole mass. After this has happened allow the tube to cool, and then break it and collect the contents. Perform the following experiments both with the original mixture and the substance obtained by heating it, noting carefully what happens in each case.

(1) Shake up with water.

(2) Test with a magnet.

(3) Pour dilute hydrochloric acid on the substance in a test-tube. Warm gently; if a gas is given off, note its smell and see if it will burn. Note carefully the kind of flame in each case. Compare what happens if the acid is poured on iron filings free from sulphur.

The results of your experiments indicate that when iron and sulphur are mixed without heating they do not undergo any chemical change:

Iron still sinks in water, and sulphur floats.

Iron is still attracted by a magnet.

Iron still acts on acid with liberation of an inflammable gas.

---

* Use the finest iron filings procurable, previously washed with caustic potash solution.

After the heating we notice that:

> The whole mass sinks in water without any separation into sulphur and iron.
>
> The whole mass is not magnetic.
>
> A different kind of inflammable gas with a smell of bad eggs is given off. It burns leaving a yellow smear in the test-tube.

We therefore conclude that a new kind of matter has been produced by the action of heat on a mixture of iron and sulphur; that is to say that a chemical change has taken place. In order to express this fact of the loss of the original properties we say that the iron and sulphur have formed a chemical compound. Thus the difference we have found so far between compounds and mixtures is that:

> A compound has quite different properties from those of its constituents (i. e. the things of which it is made up), but a mixture keeps the properties of its constituents.

As a consequence of this fact a mixture can be separated into its constituents by making use of their properties; for instance, you used the property of the solubility of sulphur in carbon disulphide to separate sulphur from iron in Experiment 7 (*a*). You could also separate these two substances by making use of their other properties: because of their different densities they would separate if shaken up with water; because iron is magnetic and sulphur not, you could use a magnet to separate them; because iron dissolves in acid and sulphur does not, you could dissolve away all the iron from the sulphur. None of these ways can be used to separate iron and sulphur after they have formed a compound.

There is another and more important difference between mixtures and compounds which you must take for granted at this stage:

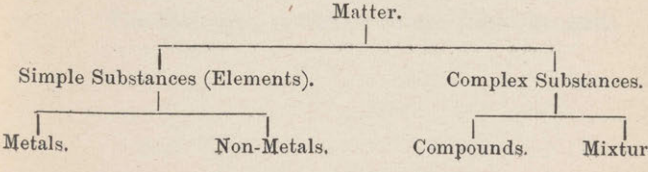
> A compound has a fixed composition but a mixture has a variable composition.

Let us take the example of iron and sulphur to make this clear. The product obtained by heating together these two substances consists of sulphur and iron. Careful experiments would show that the percentage of iron and sulphur in the compound does not vary. If you mix excess of sulphur with the iron and heat, this excess will get burnt away; and if you mix excess of iron this will be left behind, and you will notice it when you break the tube. On the other hand, if you are simply mixing iron and sulphur there is clearly no limit to the amount of either which you can use. The fact that every compound has a constant composition is called the Law of Constant Proportions. This is a law which one would naturally expect to find, and it is obviously impossible ever to prove it fully. But enough experiments have been done to prove that if there are variations in the composition of compounds, they are too small for us to notice.

It is important to notice that each constituent of a mixture behaves just as if the other constituents were not there, whereas in a compound the constituents affect one another profoundly.

The substances iron and sulphur are called *elements*, because up to the present they have never been split up into any simpler substances. Elements are either metals, like iron, or non-metals, like sulphur. We shall see later (Chapter XXX) what are the distinguishing features between these two classes.

We may therefore draw up the following table



EXAMPLES ON CHAPTER IV.

1 Show that the following results illustrate the Law of Constant Proportions:

(i) 2·6 gm. of sodium carbonate lose 1·636 gm. weight on heating.

(ii) 1·82 gm. of sodium carbonate lose 1·145 gm. weight on heating.

2 If the percentage composition of potassium chlorate is

Potassium	31·84	per cent.
Chlorine	28·98	,,
Oxygen	39·18	,,

find the weight of each of these elements in 122·5 gm. of the compound.

3 The following are some experimental results for the weights of chlorine which combine with different weights of lead. Plot them on a graph, and find from the graph a value for the weight of lead which combines with 0·71 gm. of chlorine.

Weight of lead.	*Weight of chlorine.*
0·88	0·31
1·03	0·35
1·72	0·60
2·25	0·77
2·48	0·84
2·77	0·95

V

HYDROGEN AND WATER

EXPERIMENT 15.

To examine the effect of the common dilute acids on some common metals.

You have had occasion to try the effect of dilute hydrochloric acid on zinc and on iron, and you will feel interested to know whether the inflammable gas given off in these two cases can be produced by the action of any other acid on other metals. The gas is called hydrogen.

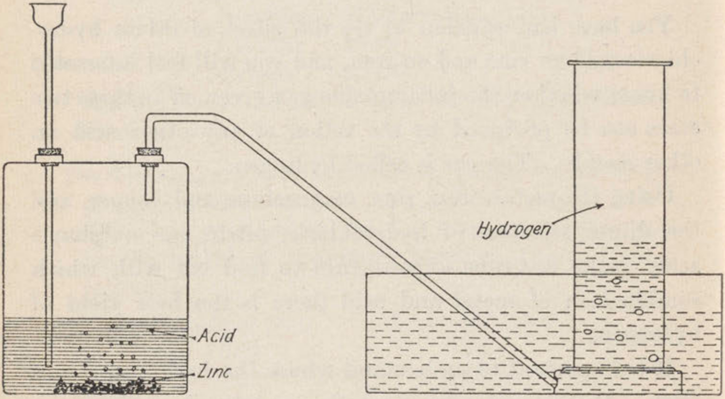
Using the metals iron, zinc, magnesium, and copper, and the dilute solutions of hydrochloric, nitric, and sulphuric acids, make test-tube experiments to find out with which combination of metal and acid there is the best yield of hydrogen.

It is important to understand where the hydrogen comes from. It does not come from the metals, since these are elements. (We have not proved this, but must take it for granted at this stage.) Nor does it come from the water with which the acid solutions have been made up, since none of these metals gives hydrogen when warmed with water. The hydrogen therefore comes from the acids.

EXPERIMENT 16.

Preparation of Hydrogen.

Set up apparatus as shown. The two-necked bottle is called a Woulfe's bottle. It is convenient to keep these bottles ready with zinc in them; the action starts as soon as the acid is poured down the thistle funnel, and when enough hydrogen has been collected the acid can be washed off the zinc, which is left in the bottle ready for the next time it is wanted. For our present purpose it will be sufficient to collect five jars of gas, and while this is being done the burners near the apparatus must be put out. If there is a jar full of water standing on the beehive shelf when the acid is first poured in, this jar will contain a mixture of air and hydrogen. This jar should be distinguished from the other four jars, which will not contain air, by means of a label.



The following experiments should be made with the jars of gas:

(1) Note the difference in what happens when a lighted taper is put to the mouth of a jar of hydrogen mixed with air and without air (labelled gas-jar).

(2) Invert a jar and thrust a lighted taper well up inside. Note carefully what happens.

(3) Invert a jar of air over a jar of hydrogen. Leave for a few minutes, and then test both jars to find if hydrogen is lighter or heavier than air.

(4) Support a jar in a retort stand in an inverted position. Remove the plate. Leave for two or three minutes and then test with a lighted taper. It will be found that the gas burns with the noise characteristic of a mixture of air and hydrogen. This shows that some of the hydrogen must have moved downwards and out of the jar, its place being taken by air: in other words, the gases have moved in opposition to gravity. The process by which gases can mix together is called *diffusion.*

EXPERIMENT 17.

Demonstration.

To collect the product obtained by burning Hydrogen.

We know by the Law of Conservation of Mass that the hydrogen is not totally destroyed when it is burnt, yet we cannot see the product of its burning as we did in the case of magnesium, when a white ash was left.

The apparatus shown in the sketch enables us to collect some of this product. The hydrogen is passed through a drying tube containing anhydrous calcium chloride,* and when all air has been displaced from the apparatus, i.e. when a test-tube of gas collected at the jet burns quietly, the gas is lit and the jet allowed to play on the surface of a retort kept cold by a stream of running water. Drops of clear liquid collect on the surface of the retort and fall into a beaker placed underneath.

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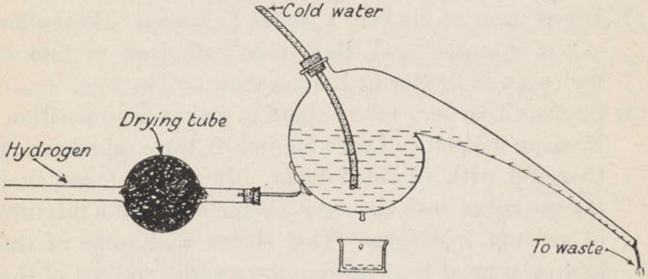
* See page 15.



You can see what a long time it would take to collect enough of this liquid to be able to test it and see if it is what it appears to be, namely, water. We should need to have enough to find

(1) If its boiling-point is the same as that of water—100° C.
(2) If its melting-point is the same as that of ice—0° C.
(3) If it has the same density as water—1 c.c. weighing 1 gm.

This has, however, been done in such a way as to leave no doubt that this liquid is water.

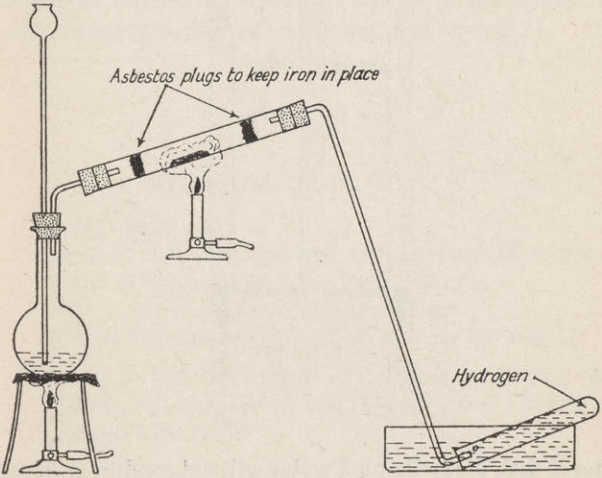
If this is the case, water must be a compound containing hydrogen, and we might therefore be able to get the hydrogen back out of water by some suitable means. This can be done by passing steam over red-hot iron filings.

Why do you think it is necessary to have a drying tube in the apparatus used above?

EXPERIMENT 18.

To obtain Hydrogen from Water.

Set up apparatus as shown, being careful to tilt the hard glass tube down towards the flask or can in which the steam is being generated, to prevent condensed steam from cracking the red-hot glass. When the water is boiling briskly and the iron is red-hot, a test-tube of hydrogen may be collected as shown, and tested with a lighted taper.

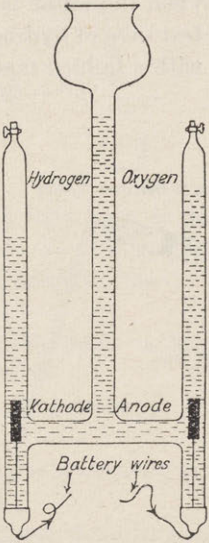


EXPERIMENT 19.

Demonstration.

The Electrolysis of Water.

We shall now try to find out what are the other constituents of water. In order to do this we send an electric current through water in a piece of apparatus called a voltameter, after Volta, the discoverer of current electricity. As a matter of fact, perfectly pure water will not conduct an electric current, and we have to add some dilute sulphuric acid to the water in the apparatus. This acid is present unchanged at the end. We shall see later (Chapter XXIII) how we could prove this experimentally. Bubbles of gas collect at both the platinum electrodes, but twice as much forms at the kathode (where the current leaves the apparatus) as at



the anode (where it enters). On testing the larger quantity of gas it is found to be hydrogen. The smaller quantity rekindles a glowing splinter, and is called oxygen.

The results of this chapter lead us to two conclusions:

(1) If water consists only of hydrogen and oxygen, as the electrolysis of water would lead one to suppose, it ought to be possible to make water by causing oxygen and hydrogen to combine together.

(2) If we find we can cause oxygen and hydrogen to combine to form water, it will follow that air must contain oxygen, since in Experiment 17 we obtained water by burning hydrogen in air.

In the next chapter we shall try the synthesis (putting together) of water from hydrogen and oxygen, and shall then be able to say whether or no air contains oxygen.

EXAMPLES ON CHAPTER V.

1 If water consists of
2 volumes of hydrogen combined with 1 volume of oxygen,
and if 1 litre of hydrogen weighs 0·09 gm.,
and 1 litre of oxygen weighs 1·44 gm.,
find the percentage composition of water by weight.

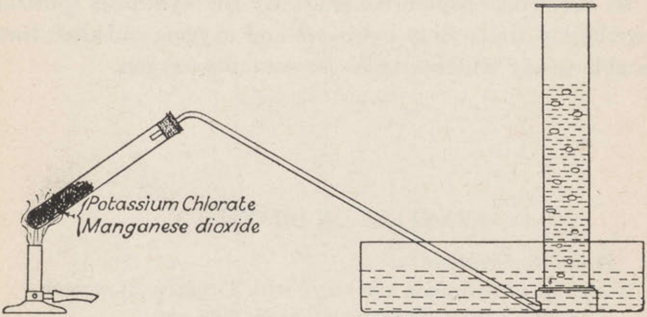
2 In order to find the volume of a flask it is weighed empty (27·496 gm.) and full of water (396·449 gm.). What is the volume of the flask?

VI

OXYGEN AND WATER
THE PROPERTIES OF GASES

Experiment 20.

Preparation of Oxygen.



Heat together in a test-tube fitted up as shown some potassium chlorate mixed with a small proportion of manganese dioxide. Let the first bubbles of gas escape, then collect several jars of gas, and burn small pieces of wood, coal, charcoal, and sulphur in them, in each case comparing the burning of the same substances in air.

EXPERIMENT 21.

Demonstration.

To make water from Hydrogen and Oxygen.

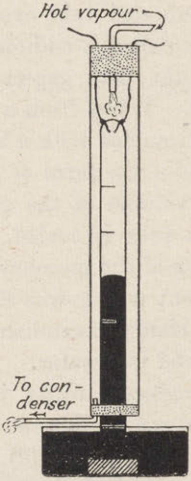
40 c.c. of dry hydrogen and 20 c.c. of dry oxygen are passed up into a graduated tube over mercury as shown. A tube of this kind is called a eudiometer tube. The tube is fitted with a platinum spark gap at the top, and rests on a thick pad of rubber. Wires from a coil lead to the spark gap. The tube is surrounded with a hot jacket so that any water formed shall be in the form of steam. After a spark has been passed the volume of the gas produced is found to be 40 c.c. If the tube is cooled, a very small drop of water forms on the top of the mercury.

This is an experiment which was first carried out by an English chemist, Sir Henry Cavendish, in 1781, who proved that the liquid produced was water.

Since we have produced water by sparking together hydrogen and oxygen, we shall now be justified in saying (1) that air contains oxygen, and (2) that water is a compound containing hydrogen and oxygen only. The compound of a single element with oxygen is called an oxide.

ℭ The Law of Gas Volumes: Molecular Weights.

Gay-Lussac, a French scientist, was very much impressed by the fact that the combining volumes of hydrogen and oxygen were exactly in the ratio of two to one. He could not think that this was a mere chance, so he made a number of experiments with other gases to find out if these also combined in simple ratios. This he found to be the case, and he expressed the result of his inquiry in what we now call Gay-Lussac's Law of Gas Volumes. This law expresses the fact that when two or more gases combine to form a compound the ratios of the combining volumes of the gases are simple whole numbers. If the compound is a gas, its volume is also connected in a very simple way with the volumes of the combining gases, e.g. 2 vols. hydrogen + 1 vol. oxygen = 2 vols. steam. In order to observe these simple ratios all the gases would of course have to be measured under the same conditions of pressure and temperature. You will have learned in Physics how greatly the volume of a gas is affected by change of pressure or temperature. The results of experiments on this subject are expressed in Boyle's Law and Charles's Law. These laws tell us that unit volume of any gas will change its volume by the same amount for any



given change of temperature or pressure. This is far from being the case with solids or liquids, some of which exhibit much more change in volume than others, but always very much less than gases.

The reason for this important difference between the gaseous and the other states of matter is the fact that in gases the molecules (cf. Chapter 1) are very much farther apart than in liquids and solids. That gaseous molecules are in constant motion follows from Experiment 16, in which we found molecules of hydrogen travelling downwards and out of the gas-jar, although they are lighter than the molecules of air which rise up and take their place. It is common knowledge, too, how the smell of a gas like coal-gas or of a vapour like petrol will fill a whole room: that is to say that the molecules of these substances travel quickly and easily through space. The molecules of solids and of non-volatile liquids do not possess this power of *diffusion* except to a very limited extent.

Gay-Lussac's discovery about volumes was made in 1805. Six years later Avogadro, an Italian scientist, suggested that equal volumes of gases, if measured under the same conditions of temperature and pressure, contain equal numbers of molecules. This statement is called Avogadro's Hypothesis (supposition) or Avogadro's Law, for although it cannot be proved that it is true by direct experiment, yet the consequences of assuming it to be true can be tested, and are found to agree with the observed facts. At this stage we will assume that Avogadro's Hypothesis is true, and make use of it in order to compare the weights of gaseous molecules. For a reason to be explained later, the molecular weight of oxygen is taken as the standard with which the other molecular weights are compared. It is given the value 32, although we might equally well have given it any other value we liked, as these so-called molecular weights are only comparisons. The actual weight of a molecule of oxygen is about 5×10^{-23} gm.

The reasoning on which we base our table of relative molecular weights is given below :

$$\frac{\text{Wt. of 1 molecule of a gas } X}{\text{Wt. of 1 molecule of oxygen}} = \frac{\text{Wt. of } n \text{ molecules of } X}{\text{Wt. of } n \text{ molecules of oxygen}}.$$

Suppose there are n molecules in a litre of the gas X; then by Avogadro's Law there will be n molecules in a litre of oxygen.

$$\therefore \frac{\text{Wt. of } n \text{ molecules of } X}{\text{Wt. of } n \text{ molecules of oxygen}} = \frac{\text{Wt. of 1 litre of } X}{\text{Wt. of 1 litre of oxygen}}.$$

But the weight of 1 litre of oxygen is 1·429 gm.

$$\therefore \frac{\text{Wt. of 1 molecule of } X}{\text{Wt. of 1 molecule of oxygen}} = \frac{\text{Wt. of 1 litre of } X}{1{\cdot}429}.$$

Now if 32 is the molecular weight of oxygen in grams,

$$\frac{\text{Molecular weight of } X}{32} = \frac{\text{Weight of 1 litre of } X}{1{\cdot}429}.$$

$$\begin{aligned} \therefore \text{Molecular weight of } X &= \frac{32}{1{\cdot}429} \times \text{weight of 1 litre of } X \\ &= 22{\cdot}39 \text{ weight of 1 litre of } X \\ &= \text{weight of } 22{\cdot}39 \text{ litres of } X. \end{aligned}$$

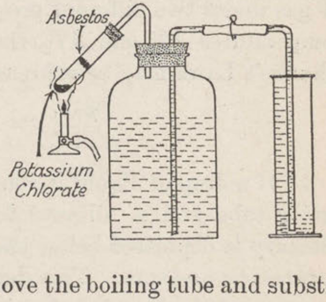
We thus see that the molecular weight of any gas can be found by weighing a known volume of the gas, and calculating the weight of 22·39 litres. The weight of the litre of oxygen given above is the weight at 0° C. and 760 mm. pressure. This is what we call 'normal temperature and pressure'. The proper definition of the molecular weight of a gas is therefore the weight of 22·39 litres of the gas at normal temperature and pressure.

EXPERIMENT 22.

To find the molecular weight of Oxygen.

If potassium chlorate is heated alone to a fairly high temperature, oxygen is given off.

Weigh a hard glass tube containing a very small quantity of potassium chlorate; in the mouth of the tube place a loose plug of asbestos. The asbestos serves to prevent particles of potassium chlorate from being driven out of the tube into the rest of the apparatus. The weighed tube is fixed on to an aspirator bottle (see diagram), whose exit tube has been filled by blowing into the inlet tube and closing the clip. Fixing on the tube will cause a slight increase of pressure inside the aspirator, which must be corrected by placing the end of the exit tube in a boiling tube containing water, held so that the level of the water in it is the same as the level inside the aspirator, and opening and closing the clip. Remove the boiling tube and substitute a 250 c.c. measuring cylinder. Open the clip and heat until about 200 c.c. of water have come over. Allow the tube to cool, keeping the end of the delivery tube under water. Replace the clip, detach and weigh the tube, take the temperature of the water in the cylinder and read its volume; read the barometer. The loss of weight of the tube gives the weight of the oxygen whose volume is the volume of the water that comes over. Correct the volume for temperature and pressure and calculate the weight of a litre of oxygen at N.T.P. The weight of 22·39 litres is the molecular weight of oxygen.



ℂ Notes on correcting the volume of a gas for temperature and pressure.

1 The absolute temperature is the Centigrade temperature + 273.

$$\text{Thus } 12^\circ \text{ C.} = 273^\circ + 12^\circ = 285^\circ \text{ A.S.}$$
$$0^\circ \text{ C.} = 273^\circ \text{ A.S.}$$
$$-40^\circ \text{ C.} = 273^\circ - 40^\circ = 233^\circ \text{ A.S.}$$

2 If v_1 and v_2 represent the volumes of a given quantity of gas under two different pressures p_1 and p_2 and absolute temperatures AT_1 and AT_2, then the results of Boyle's and Charles's Laws may be expressed thus:

$$\frac{p_1 v_1}{AT_1} = \frac{p_2 v_2}{AT_2}.$$

3 If a drop of liquid is confined over mercury in a barometer tube and is allowed to evaporate, the level of the mercury is depressed below the height which represents the barometric pressure. This depression measures the vapour pressure of the liquid under the given conditions, and if the vapour is in the presence of excess of liquid, so that the space at the top of the barometer column is saturated with the vapour, this pressure is called the saturation pressure of the liquid under the given conditions.

If, therefore, we have a quantity of gas enclosed over water, the pressure inside the vessel will be the sum of the pressure of the gas and the saturation pressure of the water vapour.

When the pressure inside the vessel is adjusted to be equal to the barometric pressure (say in a gas-jar by holding it immersed in water so that the levels are the same inside and out) then it is clear that,

pressure of gas + saturation pressure of water vapour
= barometric pressure.

i. e. pressure of gas = barometric pressure
− saturation pressure of water vapour.

The saturation pressure of water vapour at any temperature can be found by reference to the table on page 229.

4 Worked example:

Find the volume at 15° C. and 770 mm. of a quantity of dry gas which occupies 322 c.c. at 9° C. and 740 mm.

Here

$p_1 = 740$ mm.	$p_2 = 770$ mm.
$t_1 = 9°$ C. $AT_1 = 282°$ A.S.	$t_2 = 15°$ C. $AT_2 = 288°$ A.S.
$v_1 = 322$ c.c.	$v_2 = X$ c.c.

Then

$$\frac{740 \times 322}{282} = \frac{770 \times X}{288}$$

$$X = \frac{740 \times 322 \times 288}{770 \times 282}$$

$$= 316{\cdot}1 \text{ c.c.}$$

If possible logarithms should be used in working out these examples.

EXAMPLES ON CHAPTER VI.

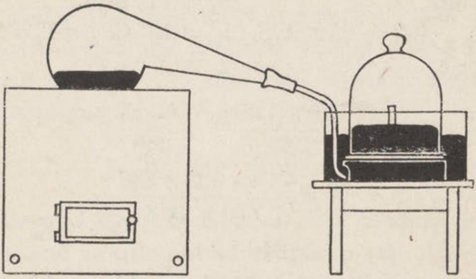
1 Find the volume at N.T.P. of 226 c.c. of air collected over water at 12° C., the barometer being at 755 mm.

2 Find the molecular weight of chlorine from the following data: 939 c.c. of the gas at N.T.P. weigh 3 gm.

VII

NITROGEN AND AIR

In Chapter VI we have shown that air contains oxygen, and now we want to find out what other gases there are present in the air, for it is clear that air must be either a mixture or a compound of oxygen with some other gas or gases; it cannot be pure oxygen or it would rekindle a glowing splinter. The behaviour of liquid air when it is evaporated proves that air is a mixture.* A gas which will not allow anything to burn in it comes off first. This gas is called nitrogen. Pure liquid oxygen is left behind. Now if air were a compound, evaporation could not split it up into its constituents any more than water is split up by evaporation into hydrogen and oxygen. If, therefore, we can remove the oxygen from a volume of air, the remaining gas will be nitrogen.



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* See also Chapter IX about the way in which air dissolves in water.

A very remarkable experiment of this kind was carried out about the year 1789 by Lavoisier, whom you will remember as the chemist who formulated the Law of the Conservation of Mass. He placed some mercury in a retort connected with a bell-jar standing over mercury. There were 50 cu. in. of air in the bell-jar and retort. The retort was heated for several days, and red scales were seen to form on the surface of the mercury. At the same time the volume of the air in the apparatus was seen to decrease (i.e. the mercury rose in the bell-jar). This continued for about twelve days, after which no further scales were formed, and the volume of the remaining gas became constant, and was found to be 42 cu. in. This gas was tested, and it was found that it would not allow things to burn in it, that is to say, it was the gas nitrogen to which we have already referred. The red scales were scraped off and heated, and they gave off a gas which measured 8 cu. in., and which, when mixed with the 42 cu. in. of nitrogen, restored the 50 cu. in. of original air. Lavoisier further weighed the mercury before and after the red scales were formed, and was able to show that the increase in weight of the mercury was equal to the weight of the 8 cu. in. of air used up.

Lavoisier recognized the gas given off when the red scales were heated as oxygen, which had been recently discovered by Priestley, an Englishman. Priestley had prepared it by heating mercury oxide (see Experiment 23) and had communicated his discovery to Lavoisier. The latter was therefore able to give a complete explanation of what had taken place in his experiment. He explained that the mercury had joined up with the oxygen of the air to form mercury calx (or mercury oxide, as we should now call it), this process continuing until all the oxygen was used up, only nitrogen being left in the apparatus. When the oxide of mercury was strongly heated, it was decomposed, and yielded up the oxygen and the mercury of which it was made.

It will probably seem surprising that heat can both cause mercury to join up with oxygen to form mercury oxide, and can then cause the mercury oxide to decompose into the elements from which it was formed. We express this fact, by saying that the action which takes place between mercury and oxygen is a reversible one. We shall find many examples of reversible reactions as we continue the study of chemistry, and we shall be able to find out what are the conditions which decide which way the action is going to take place.

We shall now pass on to some experiments which will serve to illustrate Lavoisier's theory of the composition of the air and the formation of oxides.

EXPERIMENT 23.

Heating mercury oxide: Priestley's Experiment.

Heat some mercury oxide in a hard glass tube and note the liberation of oxygen (test with a glowing splinter). Note also the formation of a mirror of mercury on the sides of the tube.

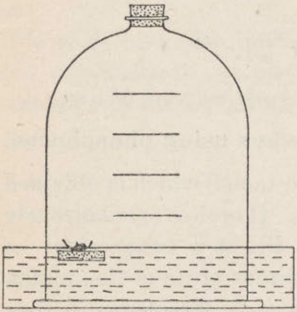
EXPERIMENT 24.

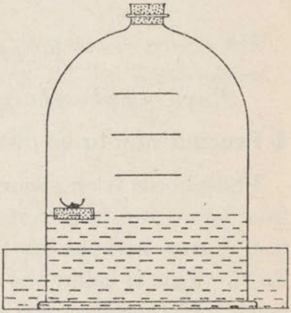
Burning phosphorus in a closed volume of air.

¶ Precautions to be observed when using phosphorus.

Phosphorus is an element (a non-metal) which is obtained from bones and from certain rocks. It ignites spontaneously (i. e. burns without having been lit) at a temperature of 34° C. This is below the normal temperature of the human body. If, therefore, you hold a piece of phosphorus in your fingers it is almost sure to ignite and cause you a painful burn. You must therefore always handle phosphorus with tongs, which are afterwards passed through the flame, so as to burn off any particles of phosphorus which might be clinging to them. The greatest care must also be taken not to drop any on the bench or on the clothes. Phosphorus is always kept under water.

Place a small piece of phosphorus on a piece of broken porcelain, and float it on a cork on water under a bell-jar. This jar should be roughly divided into five equal volumes above the water-level by means of pieces of gummed paper. Light the phosphorus by a touch with a warm glass rod, and quickly replace the stopper of the bell-jar. Note carefully how the water-level inside the jar at first sinks, owing to the expansion of the air caused by the heat of the burning phosphorus, but very soon it starts rising, and continues to do so until one-fifth of the air in the bell-jar has been used up. At this point the phosphorus stops burning, not because it is all used up, as can be easily shown by placing it in the air outside the jar, but because it has used up all the oxygen that there was in the jar. The remaining gas can be shown to be nitrogen by the usual test of seeing it put out a lighted taper. However we increase the size of the piece of phosphorus we use, we always find the same fraction, one-fifth, of the air used up in the burning, and since air is a mixture, we can therefore say that air consists of a mixture of one volume of oxygen with four volumes of nitrogen, because the volume of a mixture of gases is the sum of the volumes of its constituents. If air were a compound this would not follow, for we saw in Experiment 21 how two volumes of hydrogen combined with one volume of oxygen to form only two volumes (not three) of the compound gas, steam, so that the volume of a compound gas is not necessarily the sum of the volumes of its constituents.


Before burning


After burning

EXPERIMENT 25.

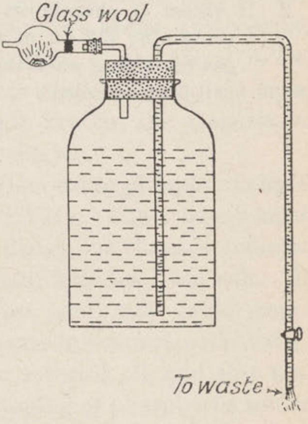
Change of weight on burning.

Lavoisier's explanation of burning leads us to expect an increase in weight due to oxygen taken up when a substance is burnt, and we can readily show this to be the case.

(*a*) A weighed piece of magnesium ribbon is burnt in a weighed crucible, the lid being held slightly above the crucible so as to allow access of air, and at the same time to prevent the loss of the white fumes produced as far as possible. The crucible and contents are weighed again when cool, and the weights tabulated.

(*b*) **Demonstration.**

A more elaborate piece of apparatus is needed to show that the substance obtained by burning phosphorus weighs more than the phosphorus. Place a piece of phosphorus in a bulbed tube containing damp glass wool as shown, and weigh. Connect the tube to an aspirator and draw a gentle current of air through the tube, at the same time warming the phosphorus until it starts burning.* When it has gone out, allow the tube to cool; weigh, and tabulate the weights.



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* The glass wool serves as a filter to prevent the fumes from passing out of the tube into the aspirator.

EXAMPLES ON CHAPTER VII.

1 The oxygen obtained by heating 2·17 gm. of mercury oxide occupied 112 c.c. at 0° C. and 760 mm. pressure.

Find (*a*) the weight of this oxygen, given that 1 litre of oxygen at N.T.P. weighs 1·43 gm.

(*b*) the percentage loss of weight of the mercury oxide.

2 If excess of phosphorus is burnt over water in a bell-jar containing 472 c.c. of air, what will be the volume of the gas remaining when the phosphorus has gone out and the bell-jar has cooled ?

VIII

OXIDES

EXPERIMENT 26.

Demonstration.

Burn pieces of charcoal, sulphur, phosphorus, sodium, calcium, magnesium ribbon, and iron wire in jars of oxygen. The first five are placed in a deflagrating spoon, ignited in the Bunsen flame, and quickly plunged into the jar of oxygen, care being taken not to let the hot bowl of the spoon touch the side of the jar. The magnesium ribbon is wound round a glass rod, and the spiral thus obtained is attached to the spoon. The iron wire is wound into a spiral, and a small piece of taper attached to the bottom of the spiral is lit. When burning iron in oxygen it is advisable to have a layer of water at the bottom of the jar to prevent the globules of molten iron oxide from cracking the jar.

The precautions to be taken when using phosphorus have already been referred to (Chapter VII). The student must now be cautioned about another dangerous element, sodium. This is a soft greyish metal manufactured from salt. It reacts very violently with water, and may cause grave injury to the eyes if allowed to come in contact with water. It is therefore always kept under mineral oil, and this fact must not be confused with the keeping of phosphorus under water.

Sodium is sometimes hard to ignite: but will burn readily if a little petrol is placed on it in the deflagrating spoon. Calcium and magnesium are also metals: calcium reacts quietly with water at ordinary temperatures: magnesium only reacts with water at a red heat (see Chapter XXXI).

In each case pour purple litmus solution into the jar, shake up, and note the result.

Burn another piece of charcoal in a jar of oxygen, and shake up with lime-water. We shall see presently what 'lime-water' is.

Lavoisier's theory of the nature of burning makes it clear that in every case when an element is burnt in oxygen an oxide is produced. Oxides can be roughly divided into three classes according to the effect they have when wet upon litmus, a purple vegetable dye:

acid oxides with water turn it red;
basic oxides with water turn it blue;
neutral oxides have no effect on it.

The oxides of carbon (charcoal), sulphur, and phosphorus are thus acid oxides. Their names are carbon dioxide, sulphur dioxide, and phosphorus pentoxide respectively. The first two are gases, and the last one is a white solid. Acid oxides are usually the oxides of non-metals. Carbon dioxide has the special property of turning lime-water cloudy. The oxides of sodium, magnesium, and calcium are basic oxides. If an element forms a basic oxide it is called a metal, and the formation of a basic oxide is the only unfailing guide which enables us to decide whether certain elements which are on the border line between the two classes are metals or not. A good many basic oxides are insoluble, and cannot therefore affect litmus. Their behaviour with acids (see Chapter XII) is then used to classify them. Iron oxide is an example of this kind.

When an acid oxide is dissolved in water its properties change and a chemical compound called an acid is formed. The dry acid oxide does not affect litmus, and the wet one does. Also heat is given out in the reaction between the oxide and the water. The solution of carbon dioxide in water contains carbonic acid, of sulphur dioxide in water sulphurous acid (not to be confused with sulphuric acid), and of phosphorus pentoxide in water phosphoric acid. Acid oxides are therefore often called acid anhydrides (i. e. acids without water). Acids produced by dissolving an acid oxide in water will clearly contain oxygen, but there are other ways of preparing acids, many of which are found not to contain any oxygen. All acids do, however, contain hydrogen.

Basic oxides also form compounds with water called bases, alkalies, metallic hydroxides or hydrates. Some of the most common bases are

sodium hydroxide, called caustic soda ;
potassium hydroxide, called caustic potash ;
and calcium hydroxide, called slaked lime or lime-water.

Since acids turn litmus red, and bases turn it blue, it ought to be possible to add a quantity of an acid to a base so that the resulting solution should not alter the purple colour of the litmus.

EXPERIMENT 27.

Formation of a Salt.

Place 25 c.c. of caustic soda (sodium hydroxide) solution in an evaporating dish, add a few drops of litmus solution, and run in hydrochloric acid from a burette until the colour is just turning pink. Note the volume of acid required. Note that when using a burette it is very desirable to have a definite way in which the readings are recorded. The one given below is satisfactory :

2nd Reading c.c.
1st Reading c.c.

Volume of acid c.c.

Now clean out the dish, add another 25 c.c. of caustic soda, but no litmus this time, and run in the same volume of acid as before. Evaporate the solution till it begins to splutter ; finish on a water-bath.

We call the white crystalline substance produced a salt because it resembles common salt. Every salt gets its name from the base and acid from which it is formed. You will remember that sodium chloride is the chemical name of common salt (see notes on Chapter II), so you will expect it to be formed when the correct or, as we call it, the equivalent quantity of hydrochloric acid is added to caustic soda solution, and this is the case. You will also guess from their names that the substances sodium carbonate, copper sulphate, potassium nitrate, ammonium chloride, potassium chlorate, and calcium sulphate are salts.* The three commonest acids are sulphuric, hydrochloric, and nitric, and their salts are called sulphates, chlorides, and nitrates respectively. The following table ought to enable you to name the salt produced when an equivalent quantity of one of the three common acids is added to any base:

ACID.	*Sodium Hydroxide.*	*Potassium Hydroxide.*	*Calcium Hydroxide.*
Sulphuric	Sodium sulphate	Potassium sulphate	Calcium sulphate
Nitric	Sodium nitrate	Potassium nitrate	Calcium nitrate
Hydrochloric	Sodium chloride	Potassium chloride	Calcium chloride

Carbonic acid is not a common acid but its salts, the carbonates, are very common. It will now be clear that when a solution of carbon dioxide (i. e. carbonic acid) is shaken up with lime-water (a solution of calcium hydroxide in water) the white solid produced must be calcium carbonate, and therefore on adding acid to the milky liquid carbon dioxide will be liberated. The carbonates behave in a special way on heating.

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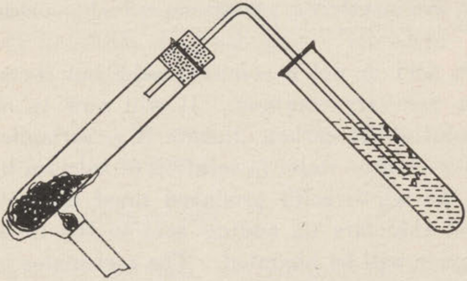
* The termination '-ate' or '-ite' always means that a salt contains oxygen.

EXPERIMENT 28.

Decomposition of Carbonates on heating.

Heat some of each of the carbonates of the following metals in a hard glass tube: copper, magnesium, lead, zinc. Arrange as in diagram to lead the gas given off into clear lime-water. It can be shown that the solid remaining in the tube after each carbonate has been heated is a basic oxide, and it is clear that in every case carbon dioxide is given off. The behaviour on heating of calcium carbonate, which is found in Nature under the forms of chalk, marble, or limestone, is particularly important. The heat of a Bunsen burner is not great enough to bring about this decomposition, which should if possible be carried out in a furnace. The process is carried out on a large scale in lime-kilns to produce the quicklime needed for mortar and other purposes.



Quicklime is the oxide of the metal calcium, and is therefore basic. It combines violently with water. This process is called slaking the lime, and results in the production of calcium hydroxide or 'slaked lime'. Slaked lime is only moderately soluble in water, but if shaken up with it a certain amount dissolves, and the clear solution obtained when the undissolved calcium hydroxide is removed by filtration is called lime-water.

EXPERIMENT 29 (*a*) and (*b*).

(*a*) Add some water to a piece of good quicklime. Note the evolution of heat; make and keep for your future use some lime-water from your specimen of quicklime. Preserve the lime-water in a stoppered bottle.

(*b*) Weigh a piece of good quicklime on a weighed watch-glass. Add to it a few drops of hot distilled water (cold water is somewhat slow to react with lime), and then as much more cold distilled water as it will take up. When the lime is completely slaked, drive off the excess water by heating in a steam-oven or on a water-bath. Alternately heat, cool, and weigh until there is no further loss in weight.

Calculate the weight of water which has combined with 100 gm. of calcium oxide to form calcium hydroxide.

EXAMPLES ON CHAPTER VIII.

1 The level of acid in a burette is 0·4 c.c. Acid is then run into 25 c.c. of alkali until the equivalent quantity (as shown by the colour change of litmus) has been added. The reading of the burette is now 23·2 c.c. Find (*a*) the volume of the given acid equivalent to 1 litre of the given alkali; (*b*) the volume of the given alkali equivalent to 1 litre of the given acid.

2 27·5 c.c. of a given acid solution containing 29·2 gm. per litre are found to be equivalent to 25 c.c. of an alkaline solution containing 35·2 gm. of alkali per litre. Find the weight of acid equivalent to 40 gm. of alkali.

IX

CARBON DIOXIDE

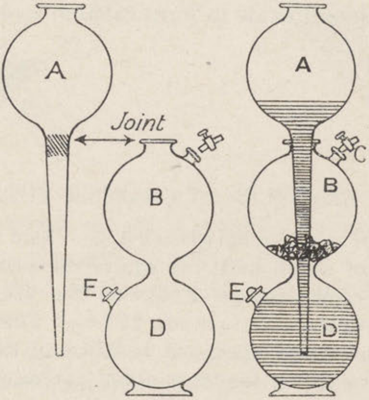
We have now found out two ways in which carbon dioxide is produced:

(1) Burning carbon in oxygen (Experiment 26).

(2) Strongly heating a carbonate (Experiment 28).

Neither of these methods is very satisfactory for yielding a quantity of the gas, and for this purpose we therefore use

(3) The action of a dilute acid on a carbonate.

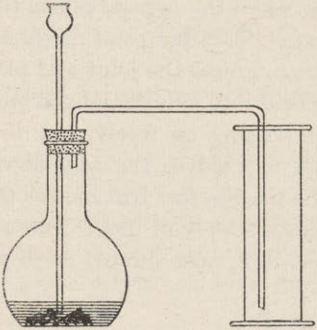


As a matter of fact any acid acting on any carbonate will produce carbon dioxide: practically we find it convenient in the laboratory to use calcium carbonate (in the form of marble) and dilute hydrochloric acid. These materials are cheap, and yield a good supply of the gas without any heating.

Kipp's apparatus is often used to provide a supply of the gas in the laboratory. It consists of a thick glass funnel-shaped reservoir A which fits by means of a ground-glass joint into another glass vessel which has a constriction in the middle. The upper bulb B has an exit tube for the gas closed by a tap C, and the lower bulb D has a stoppered opening E for use when the apparatus has to be cleaned out. To fill the apparatus, place lumps of marble in B, taking care that none fall into D, grease the joint and place A in position, open C, and pour acid into A until the marble is just covered. Gas will now be coming off freely, and if C is closed, the pressure produced in B drives the acid down into D and up into A, leaving the marble free from acid. Opening the tap C at any time yields a supply of gas. The acid used should be strong hydrochloric acid diluted with an equal volume of water.

EXPERIMENT 30.

If Kipp's apparatus is not available, use a Woulfe's bottle, or the apparatus shown, to prepare and collect a few jars of the gas. (The gas is not collected over water, since it is somewhat soluble, but by downward displacement since it is heavier than air.) Perform the following tests with the jars:



(1) Pour litmus solution into a jar and shake up: note the dark red colour produced. This shows that carbon dioxide with water forms an acid.

(2) Pour lime-water into a jar and shake up: note that the lime-water turns milky (i.e. calcium carbonate is formed).

(Note that these two results indicate that the gas produced by the action of acid on marble is the same as the gas produced when carbon is burnt in oxygen.)

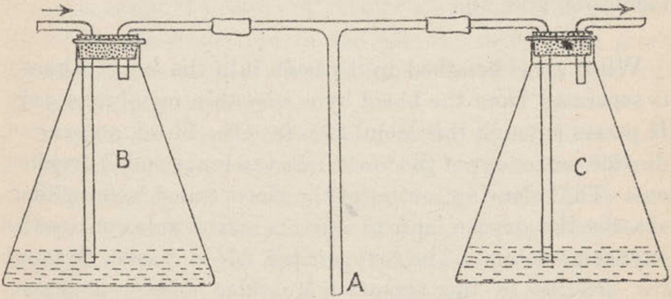
(3) Plunge a lighted taper into a jar of the gas: note that it is extinguished.

(4) Hold a lighted piece of magnesium ribbon in a jar of the gas and note that it burns brightly, forming a white ash, and depositing black specks of carbon on the sides of the jar. The burning magnesium is taking up the oxygen of the carbon dioxide to form magnesium oxide.

ℂ Carbon Dioxide in the Air.

If lime-water is left exposed to air it becomes milky. Air must therefore contain some carbon dioxide, and the following experiments will show some of the ways in which this gas gets into the air.

Experiment 31 (*a*), (*b*), and (*c*).



(*a*) Fit up two flasks containing clear lime-water as shown, and breathe in and out through the mouthpiece A. Air passes in through B, and turns the lime-water through which it passes very slightly milky. Air passes out through C, turning the lime-water through which it passes very milky.

Carbon dioxide therefore gets into the air when people (or animals) breathe out. Trees and plants also constantly produce carbon dioxide.

(*b*) Burn pieces of coal, wood, and bread in a deflagrating spoon in a gas-jar over clear lime-water. Put a glass plate on and shake up, and note that the lime-water becomes milky.

Carbon dioxide therefore gets into the air when coal, wood, or in fact any substance containing carbon is burnt.

(*c*) Dissolve 50 gm. of glucose (a kind of sugar much used in making jam and sweets) in 500 c.c. of water. Add ½ oz. of yeast, and place in a large flask fitted with a tube which dips into lime-water. Leave for some time in a warm place. Bubbles of carbon dioxide come over, and the glucose is converted into alcohol. (Note the smell of the residue in the flask.)

Carbon dioxide therefore gets into the air whenever fermentation goes on.

When air is breathed in it passes into the lungs where it is separated from the blood by a very thin membrane only. It passes through this membrane into the blood, and carbon dioxide passes out of the blood into the lungs and is breathed out. The colouring matter of the blood, called haemoglobin, absorbs the oxygen, and produces a scarlet substance called oxyhaemoglobin. The oxygenated blood passes through the arteries to the tissues. Muscular energy is always accompanied by chemical change, and the chemicals left after that change are, as it were, burnt up by combination with the oxygen of the oxyhaemoglobin. The carbon dioxide produced as a result of this combustion is absorbed by the blood, which now takes on a dark red colour, and passes back to the heart by the veins. The heart pumps the blood into the lungs to be re-oxidized.

Oxygen is therefore the part of the air which is necessary for life. When, from any cause, the lungs are unable to perform their proper function, as in pneumonia, oxygen unmixed with nitrogen is given to the patient to inhale.

Aviators and mountaineers also sometimes carry oxygen to relieve the distress caused by breathing rarefied air.

Fish obtain their oxygen from air dissolved in the water in which they live. Their breathing organs are called gills. Although air is not very soluble, such air as there is dissolved is much richer in oxygen than ordinary air. This is because air is a mixture, and its two constituents therefore keep their own solubilities. Oxygen is considerably more soluble than nitrogen, hence if air is bubbled through water a higher proportion of the oxygen than of the nitrogen will be retained by the water.

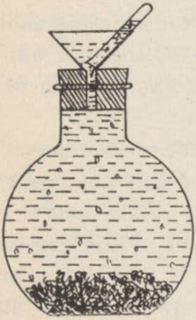
If there were no means of removing the carbon dioxide from the air it is clear that the amount of this gas present in the atmosphere would rapidly increase. As a matter of fact this is not the case. A certain amount of the gas dissolves in rain-water and in the sea, but in addition green plants remove carbon dioxide from the air and give out oxygen during the daytime.

It must not be forgotten that living plants, like most living things, are constantly absorbing oxygen from the air and 'breathing out' carbon dioxide. But, as will be seen in the next experiment, the production of oxygen in bright sunlight is quite rapid and more than compensates for the oxygen used up in the normal 'breathing' process.

EXPERIMENT 32.

Demonstration.

Place some watercress or mint in a flask filled with tap-water which contains dissolved carbon dioxide, and fitted up as shown. Leave the flask in sunlight if possible, or at least in bright daylight, for some time, when the gas collected can be tested and will be found to be oxygen. Carbon dioxide is absorbed by the leaves of plants, and by means of the green colouring matter, called chlorophyll, it is built up into starch, under the influence of light, oxygen being given off in the process. Thus green plants by taking in carbon dioxide and giving out oxygen compensate for the opposite process which occurs in the breathing of animals and plants.



ℂ Liquid and Solid Carbon Dioxide. Practical Applications of the Gas.

Carbon dioxide is produced on a large scale by the process of fermentation in breweries. The gas is collected and liquefied by compression, and may be bought in steel cylinders. If a cylinder is laid on its side and the valve opened, a jet of liquid carbon dioxide comes out. This liquid evaporates so quickly that it is immediately cooled to its freezing-point, and solid carbon dioxide, looking like snow, may be collected in a cloth. If the solid is mixed with ether it produces a freezing-mixture capable of freezing mercury.

The main use of the compressed gas is in the manufacture of mineral waters. As has been already stated, the gas is fairly soluble in water. If the gas is sent into water under pressure a much larger quantity of the gas is held in solution. When the pressure is released, effervescence is seen as the gas bubbles out of solution. This explains the behaviour of 'soda-water' when released from a bottle in which it has been kept under pressure. 'Sparklets' consist of small metal bulbs filled with the liquefied gas so arranged that the gas will be sent into water under pressure.

The action of an acid on a carbonate is used to prepare effervescent lemonade powders and 'health salts'. These consist of mixtures of some carbonate, usually sodium bicarbonate (see pp. 63 et seq.), with a solid acid, such as finely powdered citric acid. No action takes place until water is added, when brisk effervescence, due to the liberation of carbon dioxide, sets in. Baking-powder is mainly a mixture of dry tartaric acid with sodium bicarbonate, which does not react till it is moistened by the water in the dough. The bubbles of gas given off in the dough make it light and spongy. When yeast is used for making bread it sets up fermentation and carbon dioxide is liberated as in brewing.

Certain forms of fire extinguisher contain sodium carbonate solution and sulphuric acid. When the extinguisher is to be used, these are brought into contact, and the issuing gas is directed on to the fire, which it helps to smother by preventing the access of air to the flame.

Experiment 33.

To find the Molecular Weight of Carbon Dioxide.

Weigh as large a flask, corked with a sound cork, as your balance will conveniently hold. Fill it with carbon dioxide at the Kipp by passing a piece of rubber tubing from the Kipp right to the bottom of the flask and withdrawing it slowly when the flask is full, as shown by a taper held at the mouth being extinguished. Quickly cork and weigh. Find the volume of the flask by filling it with water up to the cork and measuring the volume of the water. Note the temperature and barometric pressure.

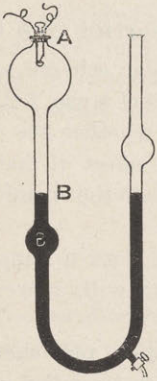
Since a litre of air at N.T.P. weighs 1·2 gm., you can calculate the weight of air in the flask, and hence the weight of the flask when vacuous. Hence you can find the weight of carbon dioxide in the flask at the temperature and pressure of the experiment. From this calculate the weight of 22·39 litres of carbon dioxide at N.T.P., which will be its molecular weight.

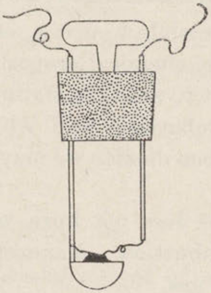
EXPERIMENT 34.

Demonstration.

To find what volume of carbon dioxide is formed from one volume of oxygen.

Some mercury is poured into the apparatus shown, the stopper A is removed and the space between A and the mercury at B filled with dry oxygen from a cylinder. To the stopper is attached a metal spoon in the bowl of which a piece of charcoal is placed. The spoon is connected to one terminal of a battery. The other battery wire is joined to a fine piece of platinum wire, which touches the charcoal and is connected to the spoon. The current is so adjusted that the platinum wire gets red-hot and ignites the carbon. The carbon burns brightly in the oxygen, and when the apparatus has cooled it is found that the level of mercury at B is unaltered This shows that the volume of carbon dioxide is equal to the volume of oxygen from which it was formed. This result is, of course, in accordance with Gay-Lussac's Law of Volumes (Chapter VI).





ENLARGEMENT OF A.

ℭ The Physical Properties of a Gas.

By the physical properties of a gas we mean :

(1) the colour.
(2) the smell.
(3) the solubility in water.
(4) the density.
(5) the ease with which it can be liquefied.

Thus if we have to describe the physical properties of carbon dioxide we should say that it is a colourless gas with a faint smell, fairly soluble in water, heavier than air, readily liquefied.

ℭ The Chemical Properties of a Gas.

It is not possible to give a similar scheme to be used in describing the chemical properties of a gas, but as a general rule it is best to start by stating whether the gas burns or supports combustion, and what effect it has on litmus. Thus for carbon dioxide we may state the chemical properties as follows :

(1) The gas does not burn, nor does it support ordinary combustion. Magnesium will, however, burn in the gas.

(2) The gas turns litmus solution red, showing that it forms a compound with water called carbonic acid. The salts of this acid are called carbonates.

(3) The gas turns lime-water milky owing to the formation of insoluble calcium carbonate.

EXAMPLE ON CHAPTER IX.

Find the molecular weight of carbon dioxide from the following data :

1·76 gm. of calcium carbonate when heated gave off 406·3 c.c. of carbon dioxide at 10° C. and 760 mm., and the remaining quicklime weighed 0·9833 gm.

X

CARBONATES AND BICARBONATES

EXPERIMENT 35.

Pass carbon dioxide for some time into lime-water until the milkiness first formed disappears. Boil some of the clear solution thus obtained, and note that carbon dioxide is liberated and a white solid deposited from the solution.

EXPERIMENT 36.

To find the percentage loss of weight of sodium bicarbonate on heating.

(*a*) **Preliminary.**

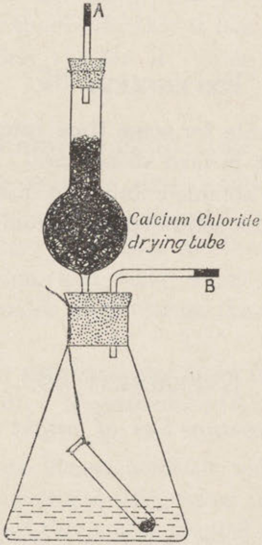
Heat some sodium bicarbonate in a hard glass tube fitted with a cork and bent tube for leading the gas given off into lime-water. Notice that carbon dioxide and a colourless liquid (water) are evolved.

(*b*) Weigh out one or two grams of sodium bicarbonate and find the percentage loss of weight on heating by the same method as explained in Experiment 9. Test the residue with acid, and note that carbon dioxide is given off. The residue is therefore a carbonate.

EXPERIMENT 37.

To find the percentage loss of weight of (a) sodium carbonate, (b) sodium bicarbonate when treated with acid.

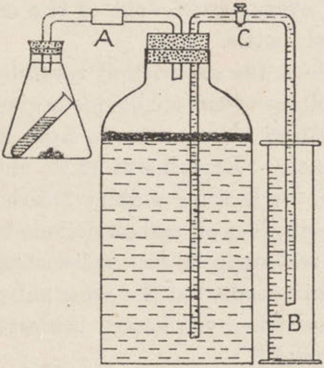
The apparatus to be used is shown in the diagram. The solid is carefully weighed in the tube which is suspended inside the flask above about 40 c.c. of dilute hydrochloric acid. Glass plugs are fastened to A and B by means of rubber tubing, and the whole apparatus is weighed. The plug at A is now removed and the solid dropped into the acid. When the reaction has ceased, the plug at B is removed and the carbon dioxide sucked out, air passing in through A to take its place. The plugs are then replaced, and the apparatus is reweighed.



EXPERIMENT 38.

To compare the volumes of carbon dioxide given off from sodium bicarbonate when treated with acid before and after heating.

Weigh out exactly 1 gm. of sodium bicarbonate into a conical flask and exactly 2 gm. into a crucible. Heat the latter for twenty minutes to low redness and allow to cool. Place inside the conical flask a test-tube containing dilute hydrochloric acid, and tall enough to be supported inside the flask without slipping. Fill the exit tube B of an aspirator by blowing through A: then close the clip C. The water in the aspirator must be covered with a layer of paraffin to prevent solution of the carbon dioxide. Fasten the flask on at A as shown, which will cause a slight increase of pressure inside the apparatus. This is corrected by placing the end of B under water in a boiling tube held so



that the level of water in it is the same as in the aspirator. By opening and closing C the pressure will automatically adjust itself.

Remove the boiling tube, substitute an empty measuring cylinder, open C, and tilt the acid on to the carbonate. When the action has finished, place the measuring cylinder so that the water-levels in it and in the aspirator are the same, keeping the end of B under water. Then close the clip, and having removed B, read the volume of water in the cylinder. It is not necessary to correct for temperature, pressure, and pressure of water vapour, since the corrections will be the same for the heated as for the unheated bicarbonate. Repeat the experiment with the heated solid, being careful to wash every particle out of the crucible into the flask with a wash-bottle.

If you have done the experiment carefully, you will find that the same volume of carbon dioxide is given off from 1 gm. of unheated sodium bicarbonate as from 2 gm. of heated sodium bicarbonate. Experiment 36 (*b*) shows us that the residue obtained by heating sodium bicarbonate is itself a carbonate, since it gives off carbon dioxide when acted upon by acid. This residue is in fact sodium carbonate, not the crystalline washing soda, but the same anhydrous carbonate that you obtained when you heated the crystals of washing soda in Experiment 9.

The difference between carbonates and bicarbonates is thus clearly that the bicarbonates contain twice as much carbon dioxide as the carbonates. We can now explain the result of Experiment 35. If we continue to send carbon dioxide into lime-water for some time, the insoluble calcium carbonate first formed is converted into soluble calcium bicarbonate. Thus the solution becomes clear again. But if it is boiled, the excess of carbon dioxide is liberated, and calcium carbonate is formed again and deposited on the sides of the vessel.

The following table should be carefully studied:

	Sod. Carb.	*Sod. Bicarb.*	*Calc. Carb.*	*Calc. Bicarb.*
Common name:	Washing soda.	Baking soda.	Chalk, marble, limestone.	—
Solubility:	Soluble.	Soluble, but less sol. than sod. carb.	Insoluble.	Exceedingly soluble.
Behaviour on heating:	Loses water and becomes anhydrous. Does not lose carbon dioxide.	Loses water and carbon dioxide and becomes anhydrous sod. carb.	Loses carbon dioxide and becomes quicklime.	Loses carbon dioxide when the solution is boiled, and calc. carb. is deposited.

EXAMPLE ON CHAPTER X.

Find from the following data the weight of potassium carbonate required to yield 44 gm. of carbon dioxide:

1·963 gm. of the carbonate when treated with acid lost 0·6156 gm. weight.

XI

HARD AND SOFT WATERS

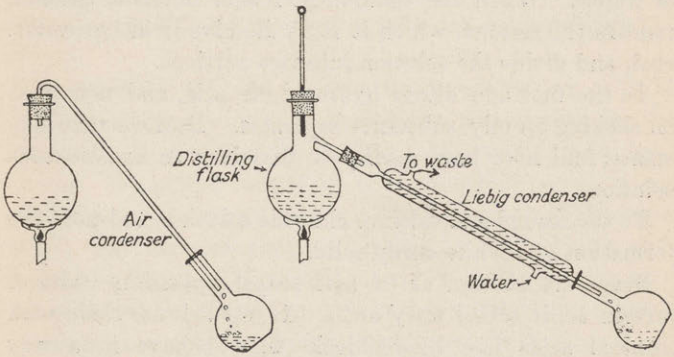
It is common knowledge that certain kinds of water which we call soft give a lather with soap much more readily than what we call hard water. This fact can be shown experimentally as follows:

EXPERIMENT 39.

To compare the amounts of soap solution required to make a lather with (a) distilled water, (b) tap-water, (c) tap-water to which a few c.c. of washing soda solution have been added.

Fill a burette with soap solution and run 1 c.c. at a time into 50 c.c. of the given water contained in a stoppered bottle. After each addition replace the stopper and shake briskly. The additions are continued until an unbroken lather which will last a minute is produced. In each of the cases note the volume of soap solution required.

The hardness of water is caused by the presence of soluble salts which react with soap and form a curd. These salts will be present in the waters of rivers which flow over soluble rocks, while rivers flowing over insoluble rocks will have soft water. The soluble salts present are often the bicarbonates of calcium and magnesium. Carbon dioxide from the air gets washed by rain into a river, making its water faintly acid. If the river then flows over rocks consisting of calcium or magnesium carbonates, a small amount of these will be dissolved as bicarbonates. Hardness due to calcium bicarbonate is, however, only temporary, for as we have already seen, if the water is boiled, the bicarbonate is converted into carbonate which comes out of solution and cannot therefore make the water hard. If chlorides and sulphates of different metals are present in the water, they will not be removed from it by boiling. They may, however, be removed by distillation. Two forms of still are shown above. In the simpler one a long tube cooled by the air is used to condense the vapour, and is called an air condenser. In the more complicated form a Liebig condenser is used. Cold water passes in at the bottom of the outer tube of the condenser and cools the inner tube before it reaches the outlet at the top of the outer tube. If water which contains chlorides or sulphates or any other dissolved mineral impurity is placed in the distilling flask, pure water will collect in the receiver.



Experiment 40.

Preparation and reactions of soap.

Warm very gently and stir in a porcelain dish a piece of lard the size of a pea with 4 c.c. of alcohol and five drops of a strong solution of caustic soda (1 gm. dissolved in 1 c.c. of water). When the solution no longer smells of alcohol, remove the residue, which is soap, dissolve it in hot water, cool, and divide the solution into two portions.

To the first add dilute hydrochloric acid, and note that on shaking an oily substance separates. Remove this substance, and note how readily it dissolves in caustic soda solution.

To the second add calcium chloride solution, and note the formation of a white curdy solid.

Soaps are sodium or (if soft soaps) potassium salts of certain acids called fatty acids. If we act on them with mineral acids like hydrochloric they behave in a way similar to that in which the carbonates act when they are acted on by acids:

acid + carbonate (salt of carbonic acid) gives carbon dioxide

and carbon dioxide + water gives carbonic acid.

Similarly

acid + soap (salt of fatty acid) gives oily substance which is the fatty acid.

The fatty acid reacts readily with caustic soda solution just as hydrochloric or any other acid would do:

hydrochloric acid + caustic soda = sodium chloride + water.
fatty acid + caustic soda = soap + water.

Some of the salts of the fatty acids, notably the calcium and magnesium salts, are insoluble in water. If we add together two solutions, one containing the sodium salt of a fatty acid, and the other the calcium salt of a mineral acid, say calcium chloride, there will be a change of partners, or as we call it a double decomposition, thus:

sodium salt of fatty acid + calcium chloride
= calcium salt of fatty acid + sodium chloride.

Since the calcium salt of the fatty acid is insoluble it will be precipitated (come down as a solid from the solution) as a curd.

If, therefore, we add soap to water containing salts of calcium or magnesium the first effect will always be the formation of a curd, as we notice when washing in hard water. When the formation of the curd is complete the soap proceeds to form a lather. The formation of the curd, which has no cleansing properties, is thus clearly very wasteful of soap. If washing soda is added to the hard water before the soap is used, it will precipitate the calcium or magnesium salts by double decomposition thus:

sodium carbonate + calcium chloride
= calcium carbonate + sodium chloride.

The calcium carbonate, being insoluble, comes out of solution and does not affect the soap in any way. Thus the sodium carbonate acts as a water softener.

If there is so much dissolved matter in a naturally occurring water as to make it taste it is called a mineral water. If you have ever been to any 'Spa', such as Harrogate, Cheltenham, or Bath, you should try to find out what particular substance dissolved in the water of that Spa has made it important.

The water of rivers and lakes is not as a rule fit to drink unless it is purified by filtration or boiling. The dissolved minerals are not injurious to health, but microscopic living organisms, called germs or bacteria, find their way into the water in dangerous numbers if the sewage on which they feed flows into a river, or if the river receives water from fields which have been manured, or from pastures. These germs cause diseases like typhoid fever. Rivers and lakes are also likely to contain a considerable amount of decayed vegetable matter, far more than would be found in the water of a spring or deep well. These waters would, however, probably contain more dissolved gases than river or lake water.

Rain-water which has fallen in the country where the air is clean is the purest kind of natural water, being, in fact, natural distilled water. If rain falls through the air of towns it will contain much dust, specks of carbon, dissolved gases from flues and chimneys, &c.

XII

SOME REACTIONS OF ACIDS, BASES, AND SALTS

We have prepared salts by adding the equivalent quantity of an acid to a base (Chapter VIII). When an acid acts on a basic oxide a salt is also produced. This action enables us to recognize as basic an oxide which is insoluble in water. We shall now try to find out how salts react with each other. We have had an example of this kind of action when we added to soap solution some calcium chloride solution (Experiment 40). You will remember that a change of partners, or double decomposition, took place thus:

sodium salt of fatty acid + calcium chloride
= calcium salt of fatty acid + sodium chloride.

EXPERIMENT 41.

Mix together some dry finely powdered lead nitrate and some sodium chloride; also some barium chloride and sodium sulphate. Note that there is no evidence of the formation of any new substance: the powders simply mix. Now make solutions of the four substances in distilled water, and add the first two and the second two together respectively. Note that in each case a white precipitate forms *immediately*, showing that a chemical change has taken place.

Salts do not in general react together unless they are in solution. If they are dissolved, their interaction is instantaneous. If by a change of partners between the metallic and acid parts of the two salts an insoluble salt would be produced, such a change of partners (double decomposition) will always take place, resulting in the precipitation of the insoluble salt.

Thus in Experiment 41, the reactions may be represented thus:

lead nitrate + sodium chloride goes to lead chloride
(insoluble)
+ sodium nitrate.
(soluble)

barium chloride + sodium sulphate goes to barium sulphate
(insoluble)
+ sodium chloride.
(soluble)

If neither of the possible products of the reaction is insoluble the action is different, and the solution will contain a mixture of salts.

Thus if we mix solutions of cupric chloride and magnesium sulphate there will be a reversible or balanced action which we can represent as follows: copper chloride and magnesium sulphate $\rightleftarrows$ copper sulphate and magnesium chloride. The reversed arrows indicate that the resulting solution when evaporated will yield some of each of the four substances mentioned.

We may summarize our results thus:

i. Salts do not react together when dry at ordinary temperatures.

ii. When in solution they react instantaneously.

iii. If by their interaction an insoluble salt can be produced, double decomposition takes place and the insoluble salt is precipitated.

iv. If no insoluble salt is produced by their interaction a balanced action takes place, resulting in a product containing a mixture of the original salts and the salts produced by a change of partners between the metal and acid parts of these original salts.

EXPERIMENT 42.

Action of Acids on Salts.

To small quantities of sodium chloride and sodium nitrate placed in dry test-tubes add cautiously enough strong sulphuric acid to occupy about 1 inch of the tube.

Caution. Strong sulphuric acid destroys cloth and wood, and burns the skin painfully. Do not let any fall on the bench nor run down the ouside of the bottle.

Note that white pungent fumes come off from the sodium chloride. A piece of blue litmus paper held in the fumes is turned red. These fumes consist of hydrochloric acid gas.

Copious brown fumes come off from the sodium nitrate and drops of liquid form at the sides of the test-tube. This liquid is nitric acid.

Caution. Never pour water into strong sulphuric acid, Sulphuric acid reacts violently with water and it may spit up into your face. Pour it cautiously right down the waste-hole.

When an acid with a high boiling-point (or, as we say, a non-volatile acid), like sulphuric acid, acts on the salt of a volatile acid, the volatile acid is liberated by double decomposition thus:

sodium chloride + sulphuric acid = sodium sulphate
(non-volatile)
+ hydrochloric acid.
(volatile)

sodium nitrate + sulphuric acid = sodium sulphate
+ nitric acid.
(volatile)

If the interacting acids are about equally volatile a balanced action will take place.

EXPERIMENTS 43 AND 44.

Action of Alkalies on Salts.

43. Mix together (*a*) dry, (*b*) in solution, some ferrous sulphate and sodium hydroxide. Note that when dry, nothing happens, but in solution a greenish precipitate of ferrous hydroxide is formed.

44. Mix together (*a*) dry, (*b*) in solution, some ammonium sulphate and sodium hydroxide. Note that when dry, nothing happens, but in solution a smell of ammonia is produced.

When an alkali acts on the solution of a salt of a metal which has an insoluble hydroxide, double decomposition takes place and the hydroxide is precipitated thus:

ferrous sulphate + sodium hydroxide
= ferrous hydroxide + sodium sulphate.
(insoluble)

When an alkali acts on the solution of a salt of a metal which forms a hydroxide easily decomposed by heat, double decomposition takes place and the hydroxide is liberated thus:

ammonium sulphate + sodium hydroxide
= ammonium hydroxide + sodium sulphate.

The ammonium hydroxide is decomposed by heat, and gives off the gas ammonia. In other cases a balanced action will take place.

We may also note how the production of the ferrous hydroxide is instantaneous, but the reaction of sodium hydroxide with lard to form soap (Experiment 40) is quite a slow action, although the interaction between soap and calcium chloride is again instantaneous.

We cannot fail to be impressed with the fact that the connexion between the acid and metal part in a salt, when in solution, seems to be very loose. We shall have more to say on this subject in Chapter XVIII.

XIII

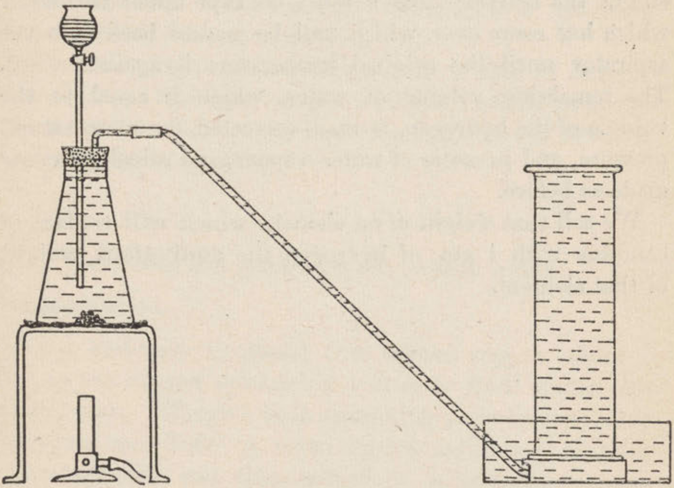
EQUIVALENT WEIGHTS

Experiment 45.

To find the weight of (*a*) *zinc,* (*b*) *magnesium,* (*c*) *aluminium which will replace 1 gm. of hydrogen from dilute acid.*

Fill a gas-jar with water, slide on a glass plate, and find the volume of water in the jar. Clean and weigh a piece of zinc foil, or of magnesium ribbon, and place it in a small tube. Invert a gas-jar full of dilute hydrochloric acid in a dish of acid. Fill the tube with water (to avoid introducing air into the gas-jar), close it with the thumb, and insert into the gas-jar. When the action has ceased, remove the tube, close the jar with a glass plate, and remove to a deep vessel of water. Adjust the jar till the levels of water inside and outside are the same, close with a glass plate, remove from the deep vessel, and find the volume of water left in the jar. Read the temperature and pressure. Find by subtraction the volume of hydrogen given off from the known weight of metal. Reduce this volume to N.T.P. and find the weight of this hydrogen, given that 1 litre at N.T.P. weighs 0·09 gm. Hence calculate the weight of metal which will replace 1 gm. of hydrogen.

In the case of aluminium the apparatus must be modified owing to the slowness with which the reaction proceeds at ordinary temperatures. In this case the weighed metal is placed in a flask, fitted as shown, which is completely filled with water, as are also the dropping funnel and the delivery tube. When all air has been removed from the apparatus, the gas-jar is set over the end of the delivery tube, strong hydrochloric acid is run from the dropping funnel into the flask, and heat is applied. When the evolution of gas has ceased, water is again run through from the dropping funnel to drive all the hydrogen into the gas-jar. Corrections for temperature, pressure, and pressure of water vapour, and calculations, are made as before.



A number of different kinds of apparatus can be used for this experiment. A graduated measuring tube is often used instead of a gas-jar. If this is the case note that very roughly 0·27 gm. of zinc, 0·075 gm. of aluminium, and

0·1 gm. of magnesium evolve 100 c.c. of hydrogen. Care must therefore be taken not to use such a big weight of metal that it will replace more hydrogen than the tube will hold.

The apparatus of Experiment 38 has much to recommend it. In this case, if heat has been applied, the apparatus must cool down to room temperature before the volume of water which has come over is read. During the cooling the end of the delivery tube B must be kept under the water which has come over, which will be sucked back into the aspirator until the original temperature is again reached. The remaining volume of water, which is equal to the volume of the hydrogen, is read, corrected for temperature, pressure, and pressure of water vapour, and calculations are made as before.

We call that weight of an element which will replace or combine with 1 gm. of hydrogen the **equivalent weight** of that element.

EXPERIMENT 46 (*a*) and (*b*).

To find the equivalent weight of oxygen.

(*a*) From previous results.

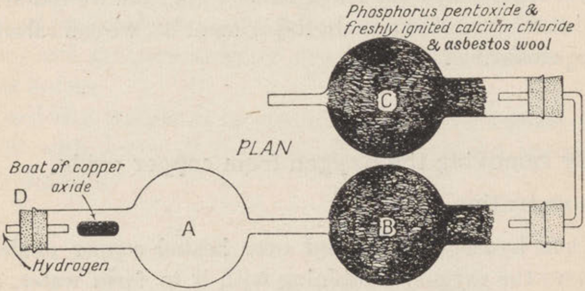
Experiment 21 showed us that 2 volumes of hydrogen combine with 1 volume of oxygen.

∴ 2 litres of hydrogen combine with 1 litre of oxygen. Since 1 litre of hydrogen weighs 0·09 gm., and we found the weight of 1 litre of oxygen in Experiment 22, we can calculate the equivalent of oxygen.

(*b*) By removing the oxygen from copper oxide.

Demonstration.

When hydrogen is passed over heated copper oxide, it removes the oxygen, combining with it to form water, and leaves copper. Weigh a boat containing pure copper oxide which has been dried by being heated for twenty minutes to low redness, and then cooled in a desiccator. Fuse together the narrow ends of two calcium chloride tubes A and B as shown. Fill another one, C, with freshly ignited calcium chloride and cotton wool. Fill B with asbestos impregnated with phosphorus pentoxide, and join to C as shown. Place the boat in position in A, close C and D with a piece of dry rubber tubing plugged with glass rod, and weigh. Remove the plugs, and pass a slow stream of hydrogen in at D. The hydrogen should be generated in a Kipp, so that its rate of flow can be regulated, and should pass through wash-bottles containing potassium permanganate solution and strong sulphuric acid to purify and dry it. When the air has been driven from the apparatus heat the boat gently. When the black colour of the copper oxide has been replaced by the reddish-brown colour of the copper remove the flame, but continue to pass hydrogen over until the apparatus is quite cold. This is necessary because the copper tends to take up oxygen from the air, i. e. the action between copper and oxygen is a balanced action. Now draw a stream of dry air through the apparatus, to displace the hydrogen. Then plug both ends with the same plugs as before and reweigh. Remove the boat and reweigh.


Phosphorus pentoxide & freshly ignited calcium chloride & asbestos wool
C
PLAN
Boat of copper oxide
D
A
B
Hydrogen

The gain in weight of the apparatus is clearly the weight of hydrogen which has joined up with the oxygen.

The loss of weight of the boat and its contents is the weight of oxygen which has combined with the hydrogen to form water. Hence the equivalent of oxygen can be calculated.

Note: the action of the hydrogen in removing the oxygen from copper oxide is called a reducing action (see Chapter XX).

The true value of the equivalent weight of oxygen is 8.

Experiment 47.

To find what weight of magnesium will combine with the equivalent weight of oxygen.

(*a*) Rough Experiment.

Carefully clean, burn, and weigh in a weighed crucible a piece of magnesium ribbon. Observe the precautions indicated in Experiment 25 (*a*). Weigh the product and calculate the required result. For various reasons this experiment will not give an accurate result, and we therefore choose another method.

(*b*) Accurate Experiment.

Weigh out in a small weighed evaporating dish a length of clean magnesium ribbon. Dissolve in the least possible quantity of nitric acid, keeping the dish covered with a watch-glass to prevent loss owing to the somewhat violent action. Wash the drops of liquid on the glass into the dish with the least possible quantity of water and evaporate on the water-bath. After a time there is no further diminution of volume and on cooling the liquid sets to a mass of crystals of magnesium nitrate.

Now heat the dish over a flame until there is no further loss of weight: that is, till the magnesium nitrate has been converted into magnesium oxide. The difference between the weight of the magnesium oxide and the weight of the magnesium used is the weight of the oxygen that has combined with it.

If you have carried out your experiments successfully you will find that the equivalent weight of magnesium (12) combines with the equivalent weight of oxygen (8). This is more than a mere coincidence, being an illustration of the Law of Equivalent Proportions, which states that equivalent quantities of different elements combine with and replace one another.

It happens in the case of metals, as we have seen in Experiment 45, that it is convenient to find what weight of the metal will replace 1 gram of hydrogen. With other elements it is often more convenient to find what weight will combine with the equivalent weight of oxygen or of chlorine, and this weight will be, as the Law of Equivalent Proportions tells us, the equivalent weight of the element.

EXPERIMENT 48.

To find what weight of lead will combine with the equivalent weight of chlorine.

Weigh a piece of clean lead foil in a weighed dish. Dissolve the metal in the least possible quantity of nitric acid as explained in Experiment 47 (*b*). To the solution of lead nitrate thus obtained add strong hydrochloric acid drop by drop until there is no further precipitation of the insoluble lead chloride. It is sometimes difficult to tell when this has happened: about 1·5 c.c. of the concentrated acid are required for every gram of lead used. Evaporate to dryness on a water-bath, and then heat over a small flame until fumes no longer come off. Weigh the dry chloride and calculate the amount of lead which will combine with 35·5 gm. of chlorine.

The hydrochloric acid and lead nitrate interact thus by double decomposition:

hydrochloric acid + lead nitrate = lead chloride + nitric acid.
(insoluble)

EXAMPLES ON CHAPTER XIII.

1 Find the equivalent of a metal of which 1·429 gm. when burnt yield 2·380 gm. oxide.

2 Find the equivalent of a metal whose oxide contains 79·9 per cent. of metal.

3 2·736 gm. of the oxide of a metal were reduced by coal-gas and 2·214 gm. of metal were obtained. Find the equivalent of the metal.

4 3·5 gm. of magnesium when treated with acid set free 0·2919 gm. of hydrogen. Find the equivalent of magnesium.

5 0·6 gm. of a metal liberated from acid 252 c.c. of hydrogen collected over water at 11° C. and 764 mm.

Calculate (*a*) The volume of dry hydrogen at N.T.P.

(*b*) The weight of this hydrogen, given that 1 litre of hydrogen at N.T.P. weighs 0·09 gm.

(*c*) The equivalent of the metal.

6 1·5 gm. of silver produced 1·995 gm. of silver chloride: find the equivalent of silver.

7 A metallic chloride contains 47·3 per cent. of metal: find the equivalent of the metal.

XIV

THE LAW OF MULTIPLE PROPORTIONS: THE ATOMIC THEORY

Experiment 49.

To find the equivalent of copper in cuprous and cupric oxides.

Close a $5 \times \frac{5}{8}$ test-tube firmly with the thumb, and heat one spot about half an inch from the bottom in the batswing flame. A small hole will blow out. Weigh the tube and introduce a small quantity of the oxide by means of a paper spill. Arrange so that the oxide lies in a thin layer on the side of the tube opposite the hole. Weigh the tube and oxide. Pass the tubing from the gas-supply well down inside the test-tube, turn the gas on gently, and ignite the gas issuing at the pin-hole. Heat the oxide in another flame until it is all converted into copper. (The coal-gas contains a high percentage of hydrogen, and acts in the same way as the hydrogen used in Experiment 46.) Continue the passage of gas through the tube while it is cooling, and reweigh. The loss in weight that has occurred is obviously the weight of oxygen that was combined with the copper left in the tube at the end of the experiment.

Use first one oxide and then the other, and calculate a value for the equivalent of copper from each result. (Remember the Law of Equivalent Proportions.)

You will find that using cuprous oxide the equivalent comes about 63, while if you use cupric oxide it is about 31·5. It thus appears that an element may have more than one equivalent. This matter was first investigated by

John Dalton, a Manchester man. He was thinking out the probable ultimate constitution of matter and started by supposing that the elements are ultimately composed of minute, indestructible particles called atoms. (Dalton did not use the word molecule, but used the word 'atom' in a wider sense than that in which we use it now.) He supposed that every atom of the same element had the same weight, and that chemical compounds were made by the union of individual atoms. The Law of Constant Proportions shows that atoms of any one kind have a fixed affinity or attraction for atoms of any other kind, for if this were not the case the constitution of compounds would vary.

Now when two atoms *A* and *B* combine to form more than one compound, as is the case with the atoms of copper and oxygen when they form cuprous and cupric oxides, Dalton supposed that something of this kind was happening: the first compound was possibly formed by the union of one atom of *A* with one atom of *B*, and the second by the union of one atom of *A* with two atoms of *B*. Now if this is the correct explanation, the ratio of the different weights of *B* which combine with a fixed weight of *A* must be a simple one. Dalton realized this and investigated the matter experimentally. He found that his results were in accordance with his hypothesis and drew up the Law of Multiple Proportions, which states that **when two elements, *A* and *B*, combine together to form more than one compound, the different weights of *B* which combine with a fixed weight of *A* bear a simple relationship to one another.**

We have not so far mentioned any standard of atomic weights, and we must now make clear what is involved in fixing those weights.

Suppose we find that the equivalent weight of an element is 36, that is to say, 36 gm. of the element combine with 1 gm. of hydrogen.

If we take the same standard for atomic weight as for equivalent weight, and call the atomic weight of hydrogen 1, we should still not be able to say that the atomic weight of the element was 36, because it would not necessarily follow that in this compound there was one atom of the element combined with one atom of hydrogen; there might be two or three. We therefore require further information about the numbers of atoms combined together in different compounds. Dalton did not possess this information, but both he and a Swedish chemist, Berzelius, were able to make some very shrewd guesses, and a table of atomic weights which was surprisingly correct was drawn up. Berzelius also simplified Dalton's idea of using symbols to represent atoms of different elements. Dalton's symbols were clumsy and Berzelius substituted letters. His system is in use to-day. For many elements the first letter stands as the symbol representing 1 atom.

Thus S means 1 atom of sulphur.
O means 1 atom of oxygen.

For others the first two letters must be taken to avoid confusion.

C means 1 atom of carbon, but Co 1 atom of cobalt.
N means 1 atom of nitrogen, but Ni 1 atom of nickel.

Others have the first letter or letters of their Latin name.

Na stands for 1 atom of sodium (Latin *natrium*).

These letters can be combined into formulae if we know the numbers of atoms which are united to form a compound.

EXAMPLE ON CHAPTER XIV.

Show that the following numbers illustrate the Law of Multiple Proportions:

Nitric oxide contains 53·33 per cent. of oxygen.
Nitrous oxide contains 36·36 per cent. of oxygen.

XV

CHLORINE

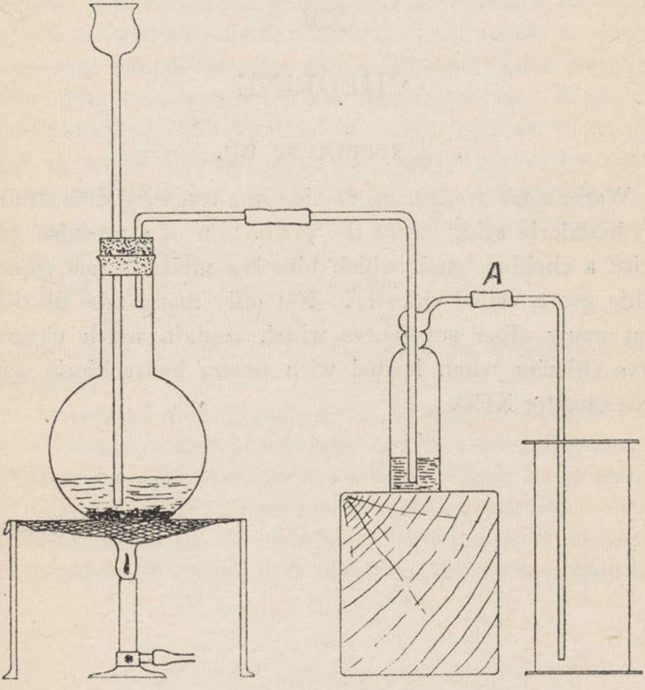
EXPERIMENT 50.

Warm some manganese dioxide in a test-tube with strong hydrochloric acid. Note the production of a greenish gas with a choking smell which bleaches moist litmus paper. This gas is called chlorine. Not only manganese dioxide but many other substances which contain much oxygen give chlorine when heated with strong hydrochloric acid (see Chapter XIX).

EXPERIMENT 51.

Demonstration.

The materials of Experiment 50 are now employed on a larger scale in order to prepare enough of the gas to make an investigation of its properties. The gas is washed free from acid by passing it through water, and is then collected by downward displacement. As the gas is somewhat soluble in water, some time elapses before the water in the wash-bottle becomes saturated with it and a steady flow is obtained. Almost any substance containing a large amount of oxygen



which it can be made to give up will react in the same way with strong hydrochloric acid, but manganese dioxide is on the whole the best and cheapest to use. The gas is extremely poisonous. It was the first 'poison gas' to be used in the Great War. Care must always be exercised in its preparation. If the student himself is undertaking this he should do it in a fume cupboard.

Physical Properties of Chlorine.

(1) Greenish colour.
(2) Choking smell.
(3) Moderately soluble; the solution is called 'chlorine water'.
(4) Heavier than air.
(5) Fairly easy to liquefy by pressure. Liquid chlorine can be bought in cylinders.

Chemical Properties of Chlorine.

The element chlorine very readily combines with other elements, forming compounds called chlorides. Many of these elements will burn in chlorine.

Chlorine reacts with the following classes of substance with production of light:
(1) metals,
(2) non-metals,
(3) hydrocarbons.

(1) A lighted piece of sodium or potassium will burn brightly in the gas, forming sodium and potassium chlorides respectively. Other ways of forming these chlorides are mentioned in Chapter XVII. In the case of finely powdered

antimony or Dutch metal (very thin foil made of copper and zinc) the action is spontaneous, i. e. the metals catch fire without being lit.

(2) Yellow phosphorus ignites spontaneously in chlorine, forming phosphorus chloride, and lighted sulphur burns in the gas with formation of sulphur chloride. A jet of burning hydrogen continues to burn in the gas with a greenish flame, forming white fumes of hydrogen chloride. To show the ease with which hydrogen and chlorine combine two gas-jars are filled, one with each gas. They are placed mouth to mouth and the plates withdrawn, and, after having been inverted a few times to mix the gases, a lighted taper is applied to each. A sharp explosion, accompanied by the formation of dense fumes of hydrogen chloride, results.

(3) Hydrocarbons are compounds containing carbon and hydrogen only. They may be solid (a wax taper), liquid (turpentine), or gaseous (coal-gas contains hydrocarbons). They burn readily with a lurid flame in chlorine, which removes the hydrogen from them, forming white fumes of hydrogen chloride, while the carbon is set free and deposited on the sides of the gas-jar. The action with warm turpentine is so violent that if a filter, paper is dipped into it, it will ignite spontaneously when thrown into a jar of chlorine.

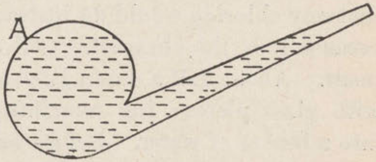
Chlorine acts on water, joining up with the hydrogen, for which it has a very strong attraction, and setting free oxygen. Chlorine water therefore gradually decomposes, the action being greatly accelerated by bright sunlight.

EXPERIMENT 52.

Demonstration.

Fill a retort with chlorine water and set it up as shown. In sunlight the chlorine water decomposes and oxygen is formed at A.

This action is made use of in bleaching. The oxygen seems to be specially active when it has just been set free from the water, and is called nascent (being born). It combines with the colouring matter to form a colourless substance. If a jar is filled with dry chlorine (dried by calcium chloride) and a piece of dry coloured material is suspended in it, there will be no bleaching action. A piece of the same cloth when wet will be rapidly bleached. Chlorine rots the fabrics that it bleaches, hence it cannot be used for delicate materials. It is, however, used extensively to bleach linen and cotton goods, the gas for this purpose being obtained from bleaching powder, which is more convenient to handle than the compressed gas. Bleaching powder is a compound of chlorine with calcium and oxygen which is formed by sending chlorine over dry slaked lime (see Chapter XXXI). In the presence of dilute acids it liberates chlorine, and even the carbon dioxide and the moisture of the air are together acid enough to liberate chlorine from it. The powder therefore always smells of chlorine. It is commonly called 'chloride of lime', and besides its use in bleaching it is a good disinfectant. The disinfecting action of chlorine is explained in exactly the same way as its bleaching action, that is to say, the nascent oxygen which it liberates from water is the disinfecting agent.



The colour and smell of the gas, and its bleaching action on moist litmus paper, are used as tests for the gas.

XVI

HYDROCHLORIC ACID: EQUATIONS

EXPERIMENT 53.

Preparation of Hydrochloric Acid.

Place 100 gm. of salt in a flask fitted up as shown for chlorine; the wash-bottle should contain about an inch depth of strong sulphuric acid to dry the gas. (Remember that sulphuric acid has a great affinity for water.) Cover the salt with 50 c.c. of water, and pour 60 c.c. of strong sulphuric acid cautiously down the thistle funnel. Note that any chloride would do instead of salt, but we use this because it is the cheapest. Collect by downward displacement. About half a dozen jars should be filled and covered with glass plates; the remaining gas should be bubbled into a beaker of water. Before leading the gas into water, remove the wash-bottle containing sulphuric acid from the apparatus and lead direct from the flask by fixing on a delivery tube at the first rubber junction. As soon as bubbles cease to come through, remove the delivery tube from the water or it will suck back. Test the gas and its solution as follows:

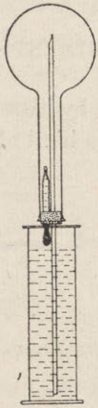
(1) Plunge a lighted taper into a jar of the gas.
(2) Remove the plate from a jar under water.
(3) Pour litmus solution into a jar.
(4) Pour strong ammonia solution from a test-tube into a jar.
(5) Pour silver nitrate solution from a test-tube into a jar.
(6) Pour some of the solution on to marble in a test-tube and test for carbon dioxide.
(7) Pour some of the solution on to zinc in a test-tube and test for hydrogen.

EXPERIMENT 54.

Demonstration.

To show the great solubility of the gas.

Fill a dry round-bottomed flask with hydrochloric acid gas. This is done by leading a rapid stream of the gas into a flask for some time (in a fume cupboard). Close the flask with a cork, through which pass a long tube drawn to a jet and a fountain-pen filler full of water. Invert the flask with the end of the long tube dipping into a jar of blue litmus solution. Squirt water from the pen-filler into the flask; the gas is so soluble that enough of it will dissolve in the small amount of water introduced to cause the litmus solution to rise right up the long tube into the flask, forming a fountain of red liquid as the colour of the litmus is changed by the wet gas.



EXPERIMENT 55.

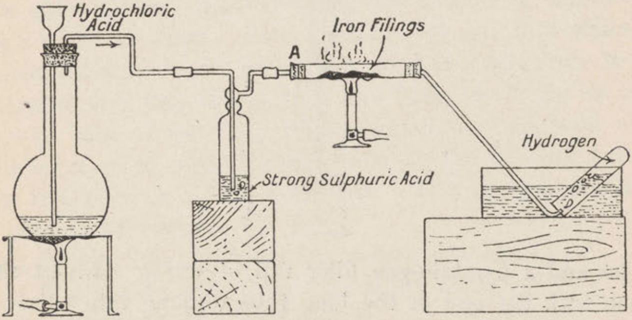
To show the presence of chlorine in the gas.

To show the presence of chlorine in the gas, pass a stream of the gas over some manganese dioxide heated in a hard glass tube. This should be done in a fume cupboard. Use apparatus like that for Experiment 56, but have a short straight tube at A and hold moist litmus paper there. Test the issuing gas for chlorine. This experiment is, in fact, only another way of carrying out Experiment 51, only in this case we use the gas itself instead of its solution. (Note that we often speak of hydrochloric acid when we mean its solution in water.)

EXPERIMENT 56.

Demonstration.

To show the presence of hydrogen in the gas, it is passed over iron filings heated in a hard glass tube, as in diagram.



A *rapid* stream of the gas is first passed through, until no air is left in the apparatus. This will be the case when bubbles cease to rise through the water in the trough. Place a test-tube full of water over the end of the delivery tube as shown, and heat the iron filings. Hydrogen is collected in the test-tube and can be tested for in the usual way.

The iron filings are converted into iron chloride (ferrous).

EXPERIMENT 57.

Demonstration.

To show that the action of strong sulphuric acid on salt is a balanced action.

Pour some of the residue from a flask in which hydrochloric acid has been prepared into a test-tube, and warm with strong sulphuric acid until the solution is clear and evolution of hydrochloric acid has ceased. The solution now contains sodium bisulphate (i. e. the sulphate with the double amount of acid, just as bicarbonate is the carbonate with the double amount of acid). Cool well, and add strong hydrochloric acid. A precipitate of sodium chloride is formed.

We may represent the action thus :

$$\text{sulphuric acid} + \text{sodium chloride} \rightleftarrows \text{hydrochloric acid} + \text{sodium bisulphate.}$$

The way the action takes place depends on the conditions.

Thus in making hydrochloric acid the reaction proceeds from left to right, because the hydrochloric acid, being a gas, is removed as fast as it is formed. When hydrochloric acid is added to a strong solution of sodium bisulphate, the sodium chloride, being only sparingly soluble in strong hydrochloric acid (test this by experiment) separates from the solution and so cannot 'react back'.

¶ Physical Properties of Hydrochloric Acid.

(1) Colourless.
(2) Pungent smell.
(3) Very soluble, and therefore fumes in moist air, because it dissolves in droplets of moisture.
(4) Heavier than air.

¶ Chemical Properties of Hydrochloric Acid.

(1) The solution of the gas in water turns litmus red.
(2) The gas does not burn or support combustion.
(3) The solution of the gas when acted on by certain metals (Experiment 15) gives off hydrogen.
(4) The solution of the gas sets free carbon dioxide from carbonates (Chapter IX).
(5) The solution of the gas reacts with alkalies to form salts called chlorides (Chapter VIII).

The main use of the gas is for the preparation of chlorine for making bleaching powder.

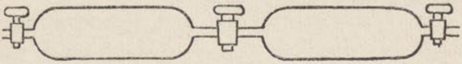
¶ Composition and formula of Hydrochloric Acid.

Since hydrochloric acid is formed when a jet of hydrogen is burnt in chlorine, it is clear that the acid must consist only of these two elements. Electrolysis of the acid in solution in a voltameter resembling the one used in Experiment 19, but with carbon electrodes (platinum would be attacked by the chlorine), results in the liberation of equal volumes of the gases at the two electrodes.

Experiment 58.

Demonstration.

If a tube of the kind shown below is filled on one side of the central stopcock with chlorine and on the other with an equal volume of hydrogen, and the gases allowed to mix for a day in diffuse daylight, a volume of hydrochloric acid which completely fills the tube is produced. This can be shown in the following manner. If an end of the tube is opened under mercury, no mercury enters the tube, showing that it is full of gas at atmospheric pressure, and if an end of the tube is opened under water, the whole tube becomes filled, showing that there is no residual chlorine or hydrogen, but that the tube contains hydrochloric acid gas.



We may therefore say that

1 volume of hydrogen reacts with 1 volume of chlorine and yields 2 volumes of hydrochloric acid.

Therefore by Avogadro's Law we may say that

1 molecule of hydrogen reacts with 1 molecule of chlorine and yields 2 molecules of hydrochloric acid gas.

Therefore since each molecule of hydrochloric acid must contain some hydrogen and some chlorine, the molecules of each of these gases must contain at least two atoms. No reactions of the gases hydrogen and chlorine are known in which the volume relations are such that we have to suppose that their molecules contain more than two atoms. We therefore represent the molecules of hydrogen and chlorine by the symbols H_2 and Cl_2.

We can now write our first chemical equation:

$$H_2 + Cl_2 = 2HCl,$$

where HCl is the formula of a molecule of hydrochloric acid. This equation expresses the following facts:

(1) 1 molecule of hydrogen combines with 1 molecule of chlorine, and yields 2 molecules of hydrochloric acid.

(2) 1 volume of hydrogen combines with 1 volume of chlorine, and yields 2 volumes of hydrochloric acid.

(3) If we know the atomic weights of hydrogen and chlorine (1 and 35·5) it also tells us that

2 gm. of hydrogen combine with 71 gm. of chlorine and yield 73 gm. of hydrochloric acid.

EXAMPLE ON CHAPTER XVI.

Find the percentage composition of hydrochloric acid from the formula.

XVII

THE CHLORIDES: VALENCY

In considering the chlorides we must bear in mind that not only are they the compounds of the elements with chlorine, but also the salts of hydrochloric acid. The chlorides of the non-metals do not concern us at this stage; they are for the most part highly unstable substances which are readily decomposed by the moisture in the air, giving off fumes of hydrochloric acid. The chlorides of the metals are extremely important substances. Many metals have two chlorides, in which case the chloride containing the higher proportion of the metal is given the termination '-ous', and the other one the termination '-ic'. Thus ferrous (iron) chloride (Experiment 56) contains a higher percentage of iron than ferric chloride.

If we know the formula of a compound made up of two elements we can tell how many atoms of one of its constituents will combine with 1 atom of the other. Thus from the formula HCl we see that 1 atom of chlorine combines with 1 atom of hydrogen. When 1 atom of an element combines with 1 atom of hydrogen that element is said to be **monovalent** or to have **unit valency**. In general we define the valency of an element as the number of monovalent atoms with which 1 atom of that element will combine. For example, the formulae that express the composition of the chlorides of iron are $FeCl_2$ (ferrous chloride) and $FeCl_3$ (ferric chloride) respectively, from which we gather that iron can be both divalent and trivalent.

A knowledge of the valency of an element in any given compound with an element of known atomic weight and of its equivalent weight in that compound would enable us to fix its atomic weight.

For suppose in hydrogen oxide (water) we knew:

(1) that the valency of oxygen is 2 (i. e. that 1 atom of oxygen combines with 2 atoms of hydrogen);

(2) that the equivalent weight of oxygen was 8 (i. e. that 8 gm. of oxygen combine with 1 gm. of hydrogen).

Then 2 gm. of hydrogen are combined with 16 gm. of oxygen.

But 2 atoms of hydrogen are combined with 1 atom of oxygen.

∴ The atom of oxygen must weigh 16 times the weight of the atom of hydrogen: that is, the atomic weight of oxygen is 16 if the unit of atomic weight is the weight of the atom of hydrogen.

And in general it must follow by precisely similar reasoning that

$$\text{Equivalent Weight} \times \text{Valency} = \text{Atomic Weight.}$$

ℭ Preparation of Metallic Chlorides.

(1) Direct combination of the metal with chlorine.

Since chlorine attacks almost every metal, this method is in theory applicable to the preparation of almost any metallic chloride. In practice, however, the method is rarely used because it is inconvenient. An illustration of preparing chlorides by this method is the burning of different metals in chlorine (see Chapter XV). We may now write the equation for the burning of sodium in chlorine, which results in the formation of sodium chloride whose formula is NaCl.

$$Na + Cl = NaCl.$$

This equation does not, however, represent the fact that there are two atoms in the molecule of chlorine, and we shall therefore be more correct if we write it thus:

$$2Na + Cl_2 = 2NaCl.$$

(2) Action of acid, in solution or gaseous, on the metal.

Magnesium chloride could be made by this method. The metal would be dissolved in a solution of hydrochloric acid, and, on crystallizing out the solution, magnesium chloride would be obtained.

$$Mg + 2HCl = MgCl_2 + H_2.$$

In Experiment 56 we had an example of making a chloride by passing the gas over the metal.

$$Fe + 2HCl = FeCl_2 + H_2.$$

The direct action of the acid on the metal cannot be used for the preparation of the chloride if either:

(1) The metal is not attacked by hydrochloric acid, e.g. copper.

(2) The action is too violent, as would be the case if the solution of the acid were poured on sodium.

(3) Action of acid on the oxide, hydroxide, or carbonate of the metal.

These three compounds are chosen because they yield with hydrochloric acid solutions from which the chloride can be obtained pure by a simple evaporation.

e. g. cupric oxide and hydrochloric acid give cupric chloride and water and nothing else.

$$CuO + 2HCl = CuCl_2 + H_2O.$$

Sodium hydroxide and hydrochloric acid give sodium chloride and water and nothing else.

$$NaOH + HCl = NaCl + H_2O.$$

Calcium carbonate and hydrochloric acid give calcium chloride, water, and carbon dioxide, which is driven off from the solution on boiling.

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

(But calcium nitrate and hydrochloric acid would give on evaporation a mixture of the chloride and nitrate, i. e. a balanced action takes place.)

(4) Precipitation of an insoluble chloride.

Since lead, silver, mercurous and cuprous chlorides are the only insoluble ones, this method has only a limited application. Either the acid itself (Experiment 48) or a solution of a soluble chloride can be used to precipitate the insoluble chloride, which can then be filtered off, washed and dried.

Of all the chlorides sodium chloride is the most important. It is never prepared by any of the above methods, because it occurs plentifully in nature. In England it is mined as rock-salt, or else holes may be bored in the salt deposit and water be forced down so that it dissolves the salt. The brine is then pumped up and evaporated to dryness.

Round the shores of the Mediterranean salt is obtained by the evaporation of sea-water in shallow lagoons. The final driving off of the last traces of water is carried out over a fire. In very cold countries use is made of the fact that when salt water freezes the ice is free from salt, which is left in the water below the ice. Thus by repeatedly freezing the same lot of sea-water a very strong brine suitable for evaporation over the flame can be obtained.

EXPERIMENT 59.

Tests for Chlorides: use sodium chloride.

(1) Add to the dry chloride strong sulphuric acid. Fumes of hydrochloric acid will be given off on heating. These fumes can be recognized by the fact that they turn blue litmus paper red, and give dense white fumes of ammonium chloride with a drop of ammonia solution held on the end of a glass rod at the mouth of the tube. The addition of a little manganese dioxide to the chloride and acid results in the production of chlorine, formed by the action of the hydrochloric acid on the manganese dioxide.

(2) Use a solution of the chloride to see if it will give the characteristic precipitate with a solution of silver nitrate.

EXAMPLES ON CHAPTER XVII.

1 Find the percentage compositions of ferrous and ferric chlorides from the formulae ($FeCl_2$, $FeCl_3$).

2 From the equation

$$2Na + Cl_2 = 2NaCl,$$

find the weight of sodium chloride which can be formed from:

(*a*) 46 gm. of sodium.
(*b*) 1 gm. of sodium.

3 From the equation

$$Mg + 2HCl = MgCl_2 + H_2,$$

find the weight of hydrogen liberated by 1 gm. of magnesium. Find also the volume occupied by this hydrogen, given that 1 litre of hydrogen at N.T.P. weighs 0·09 gm.

[Look up Atomic Weights on page 229.]

XVIII

ACIDS, BASES, AND SALTS: ELECTROLYSIS

EXPERIMENT 60.

Demonstration.

Connect up an electrolytic cell (two pieces of copper foil dipping in a beaker is a simple form) in series with an electric lamp to the main if the current is direct. If this is not available an accumulator and miniature lamp will answer the purpose very well.

Half fill the cell with the following substances in turn, and note in which cases a current flows (as shown by the lamp glowing). (1) Dry sodium chloride, (2) distilled water, (3) solution of sodium chloride, (4) dilute solution of sodium hydroxide, (5) dilute solution of hydrochloric acid, (6) solution of sugar, (7) solution of soap.

Dry the cell thoroughly by rinsing with alcohol and ether, and then try (8) toluene (a liquid obtained by heating coal when coal-gas is made), (9) a solution of hydrochloric acid in toluene.

It appears from the results of the above experiments that solutions of acids, bases, and salts in water conduct electricity while other solutions do not. We notice in this connexion that soap behaves like a salt, as we should expect. We therefore call these three classes of substance electrolytes. We also note that the passage of an electric current through the solution of an electrolyte (called 'electrolysis') is always accompanied by decomposition of the dissolved substance. The products of decomposition, however, only appear at the electrodes and not throughout the solution. We shall presently state the theory which is put forward to explain these facts.

ℂ Faraday's Law of Electrolysis.

Faraday set up a number of water voltameters in series, and passed a current through them (Experiment 19). After some time he found that the quantity of hydrogen liberated was the same in each voltameter, although these voltameters were very different from one another. When he halved the current, or halved the time for which the current was passed, he only got half the quantity of hydrogen in each voltameter, from which he concluded that the quantity of a substance which separates out at an electrode is proportional to the quantity of electricity (current × time) passing through the solution.

He next joined up in series a number of voltameters containing solutions of different metallic salts, and found that the weights of metal deposited on the kathodes of these voltameters were proportional to their chemical equivalents.

These two results are conveniently expressed as one statement called Faraday's Law. The quantity of a substance which separates out at an electrode is proportional to the quantity of electricity and to the chemical equivalent of the substance liberated.

The theory put forward to explain these facts is called the Ionic Theory.

When an acid, a base, or a salt is dissolved in water it is immediately split up into two parts called ions, which bear opposite charges of electricity. When an electric current is applied to such a solution, the ions move toward the electrodes of opposite sign, give up their charges of electricity there and are either liberated, or else react with the water or with the material of the electrodes. The metals and the gas hydrogen always appear as the kathode, which is the electrode through which the current leaves the solution, and is hence the *negative* electrode. Metal ions and hydrogen ions are therefore supposed to be *positively* charged. Non-metals (and non-metallic groups like SO_4 in sulphuric acid H_2SO_4 and the sulphates) are negatively charged, and are liberated at the anode or positive electrode where the current enters.

The ions provide the mechanism whereby the current is transmitted through the solution, for the positively charged ions (kathions) hand positive electricity to the kathode, and the negatively charged anions take positive electricity from the anode. If there are no ions the current cannot pass: and acids, bases, and salts are the only three classes of substance which are ionized: hence these are the only classes of substance whose solutions are conductors of electricity. Whenever the solution of an acid is electrolyzed, hydrogen is liberated at the kathode; in other words, the positive ion of any acid is hydrogen ion. The negative ion is different for every acid, and when it loses its charge at the anode very frequently reacts with the water of the solution in such a way as to re-form the acid, and to set free oxygen. Thus the negative ions of the three common acids are called sulphate ions, chloride ions, and nitrate ions respectively. Sulphate and nitrate ions attack water, taking up the hydrogen to form sulphuric and nitric acids, oxygen being thus set free. Expressed by means of atomic symbols (formulae) these changes are shown thus:

$$\underset{\text{sulphate ion}}{SO_4} + 2H_2O \rightarrow 2H_2SO_4 + O.$$

$$\underset{\text{nitrate ion}}{NO_3} + H_2O \rightarrow HNO_3 + O.$$

Chloride ion does not attack water, and is therefore either liberated as chlorine gas at the anode, or attacks the material of the anode, as the case may be.

The property of furnishing hydrogen ion when dissolved in water is the one property which is common to all acids, and we therefore define an acid as a substance whose solution in water contains two kinds of ions, one of which is hydrogen ion. Since, then, a solution of any acid contains hydrogen ions we should expect that all such solutions should contain some properties in common, and this we find to be the case. These common properties are, of course, the properties of the hydrogen ion. They are as follows:

(1) Sour taste.
(2) Corrosive action.
(3) Turning litmus solution red.

There are also three reactions exhibited by most acids:

(1) Action on metals with liberation of hydrogen.

(2) Action on carbonates with liberation of carbon dioxide.

(3) Action on bases with formation of a salt.

The strength of an acid depends on the percentage of its molecules ionized in water. Bases also have a characteristic ion called hydroxyl ion, but it is not easy to recognize like the hydrogen ion, since free (unchanged) hydroxyl is never liberated. It is a negative ion containing hydrogen and oxygen (OH), and when it loses its negative charge it forms water and liberates oxygen, thus:

$$\begin{array}{l} \mathrm{O\,H} \\ \mathrm{O\,H} \end{array} \rightarrow \mathrm{O} + \mathrm{H_2O}$$

The other ion in a solution of a base is a metallic ion. This will be liberated unchanged on electrolysis if the metal does not act upon water; if it does, as in the case when the sodium ion loses its charge at the kathode, we get the usual products of the action of a metal on water, namely a hydroxide (or oxide) and hydrogen. A base is defined as a substance whose solution in water contains two ions, one of which is hydroxyl, and the other a metallic ion.

The properties of hydroxyl ion are:

(1) Bitter taste.
(2) Corrosive action.
(3) Slimy feeling.
(4) Turns litmus solution blue.

The following reactions are exhibited by most bases:

(1) Action on animal oils and fats forming soaps.
(2) Action on acids forming salts.

The strength of a base depends on the percentage of its molecules ionized. Water is ionized to an extremely small extent, and it splits up into two ions, hydrogen and hydroxyl. There will clearly be the same number of hydrogen and hydroxyl ions in any volume of pure water. If by any means the number of hydrogen ions is made greater than the number of hydroxyl ions, the solution will have an acid reaction to litmus, and if the number of hydroxyl ions is made greater than the number of hydrogen ions, the solution will have an alkaline reaction.

We shall now apply the ionic theory to the explanation of salt formation as carried out in Experiment 27. When the intermediate colour of the litmus has been attained, the solution contains the four following ions in equivalent quantities: Hydrogen, sodium (both positive), hydroxyl, chlorine (both negative). Note that the ions are present, although no electric current is being sent through. As in electrostatics, like charges repel one another, and unlike attract. Thus the possible combinations are hydrogen with hydroxyl or chlorine, and sodium with hydroxyl or chlorine. Hydrogen and hydroxyl together form very slightly ionized water, and thus practically all the hydrogen and hydroxyl ions are removed from the solution, leaving the only possible product, namely sodium chloride, which appears in its usual form as soon as the water has been driven off.

ℭ **Explanation of double decomposition** (Experiments 41 to 44) **on the Ionic Theory.**

In the case of the mixture of solutions of lead nitrate and sodium chloride, the ions present are

lead and sodium (both +)
chloride and nitrate ion (both −)

Whenever a lead ion meets a chloride ion they are attracted, and a molecule of lead chloride is formed, which being insoluble is not ionized. The formation of countless molecules of lead chloride in this manner results in the white precipitate of lead chloride.

A similar explanation applies in any case where precipitation results from adding together acids, bases, or salts.

The liberation of a volatile acid (e.g. hydrochloric acid) from its salts by a non-volatile acid takes place because as soon as a molecule of the volatile acid is formed it moves rapidly out of the solution, and hence is not again split up into its ions.

We define a salt as a substance whose solution in water furnishes two ions, neither of which is either hydrogen or hydroxyl. Its positive ion is metallic, and its negative ion is the negative ion of the acid from which it is derived, and from which it partly takes its name, as previously explained.

EXAMPLES ON CHAPTER XVIII.

1 Silver chloride contains 75·26 per cent. of silver. Excess of chloride ion was added to 10 c.c. of silver nitrate solution and the precipitated silver chloride was filtered off, dried, and found to weigh 1·435 gm. Calculate the weight of silver ion per litre of the silver nitrate solution.

2 If 0·1072 gm. of copper is deposited from copper sulphate solution by the passage of a given quantity of electricity, what weight of silver will be deposited from silver nitrate solution by the passage of the same quantity of electricity? [Equivalent of copper = 31·75; of silver = 108.]

3 If 1 ampere deposits 4 gm. of silver in 1 hour, what weight of hydrogen will be produced by half an ampere in 1 day?

4 A current of 2·4 amperes decomposes 4 gm. of water in 5 hours. Find the weight of hydrogen produced by 1 ampere in 1 second.

XIX

A FORMULA FOR WATER: FIXING ATOMIC WEIGHTS

We can now use the results of Experiment 21 to find a formula for water. This experiment showed us that:

2 volumes of hydrogen + 1 volume of oxygen
= 2 volumes of steam.

Applying Avogadro's Law we may therefore say that:

2 molecules of hydrogen + 1 molecule of oxygen
= 2 molecules of steam.

Now since each molecule of steam must contain some oxygen, the molecule of oxygen must contain at least 2 atoms. Also we have shown (Chapter XVI) that the molecule of hydrogen contains 2 atoms.

We may therefore write: $2H_2 + O_2 = 2M$, where M is the formula for 1 molecule of steam, whence it is clear that M, the formula for water, is H_2O.

We are now in a position to explain why the molecular weight of oxygen (32) is taken as standard of molecular weights. Hydrogen was originally taken as standard because it is the lightest element known, with atomic weight 1 and molecular weight 2. We have just shown that in water 2 atoms of hydrogen are combined with 1 atom of oxygen, and a synthesis of water on the lines indicated in Experiment 46 (*b*) shows that 2 gm. of hydrogen are combined with 16 gm. of oxygen (very nearly); that is to say that the atomic weight of oxygen is very nearly 16. It is found to be better to take oxygen as having an atomic weight of quite 16 (which makes the atomic weight of hydrogen be not exactly 1) and treat oxygen as the standard, because more elements will combine with oxygen than will combine with hydrogen. The numerical values of the atomic and molecular weights are very nearly the same whether we take oxygen or hydrogen as the standard. All the common elements, except bromine and fluorine, form oxides, many of which can readily be obtained pure, and whose composition can consequently be accurately determined. Only a few elements, on the other hand, form compounds with hydrogen, and many of these do not, for various reasons, lend themselves to accurate analysis.

Avogadro's Law supplies us with a standard for fixing the atomic weight of an element by finding the molecular weights of its volatile compounds as explained in Chapter VI. Each of these volatile compounds must then be subjected to an analysis, and the amounts of the element whose atomic weight is being sought present in 1 gm. molecular weight of each compound written down. Suppose, for instance, that we wanted to know the atomic weight of nitrogen. We might find its molecular weights and those of nitric and nitrous oxides and ammonia, which are all gases. We should then have to analyse each of these compounds, and write down the results as shown:

Gas.	*Mol. Wt.*	*Weight of Nitrogen in 1 gm. Mol. Wt.*
Nitrogen	28	28
Nitric oxide . . .	30	14
Nitrous oxide . . .	44	28
Ammonia . . .	17	14

This table could be extended very much by adding to it the results obtained from other compounds of nitrogen, but we should always find that the weight of nitrogen present in one gram molecular weight of any compound was either 14 or else a multiple of 14. We therefore take 14 to be the atomic weight of nitrogen, since it is the smallest weight of the gas which enters into combination with other elements.

If a sufficient number of volatile compounds is not known, other methods, which need not be described here, are available for finding the molecular weights of non-volatile compounds. We must now make clear thc difference between a molecule, an atom, and an ion.

A molecule is the smallest part of an element or compound which is capable of existing independently and of retaining the properties of that element or compound. It may consist of one or more atoms, which may be all alike (as is the case in the molecules of elements) or different (as is the case in the molecules of compounds). These atoms may become divided from one another in the processes of chemical change, but they cannot exist independently once those changes are over. As we have said already, an atom is the smallest particle of an element that can take part in a chemical change. An ion is a charged atom or group of atoms, formed when an electrolyte is dissolved in water.

We shall conclude the chapter by proving that the Vapour Density of a gas is half its Molecular Weight. Since gases are so very light it is usual to take hydrogen as the standard of reference instead of water, as is the case with solids and liquids. The Vapour Density of a gas X

$$= \frac{\text{Weight of 1 litre of the gas at N.T.P.}}{\text{Weight of 1 litre of hydrogen at N.T.P.}}\cdot$$

$$= \frac{\text{Weight of 22·39 litres of } X}{\text{Weight of 22·39 litres of hydrogen}}\cdot$$

$$= \frac{\text{Weight of 22·39 litres of } X}{2}$$

$$= \frac{\text{Molecular Weight of } X}{2}\cdot$$

If we make a list of solid elements and write down their atomic weights and their specific heats, we shall find that if we multiply these two numbers together the answer comes very near 6·4: thus

for iron,

Atomic Weight = 56. S. Ht. = 0·112, product = 6·3.

for zinc,

Atomic Weight = 65·4. S. Ht. = 0·093, product = 6·1.

for gold,

Atomic Weight = 197. S. Ht. = 0·032, product = 6·3.

Dulong and Petit first discovered this relationship, and they drew up what is known as Dulong and Petit's Law: The specific heat of a solid element × its atomic weight is a constant (roughly 6·4).

Thus if we know the specific heat of an element, this Law will give us a rough value for the atomic weight. And since the chemical equivalent can be determined with great accuracy, and the atomic weight is the chemical equivalent multiplied by some simple whole number (the valency), the rough value of the atomic weight obtained from Dulong and Petit's Law will enable us to assign a value to the valency, and thus lead to the determination of the accurate atomic weight.

EXAMPLES ON CHAPTER XIX.

1 Write down the meanings of the equation

$$2H_2 + O_2 = 2H_2O.$$

2 0·1036 gm. of ether occupy 32·7 c.c. at 12° C. and 749 mm. What is the volume of this ether at N.T.P.? What is the weight of a litre of ether at N.T.P.? What is the Vapour Density of ether? (1 litre of hydrogen at N.T.P. weighs 0·09 gm.) What is the molecular weight?

XX

OXYGEN (REVISION); PEROXIDES; OXIDATION AND REDUCTION; HYDROGEN (REVISION)

EXPERIMENT 61.

Heat a small quantity of each of the following substances in a hard glass tube. In each case test for oxygen, and note whether a very high temperature has to be reached before the gas comes off:

barium peroxide.
potassium chlorate.
potassium nitrate.
potassium permanganate.

Although all the substances heated in Experiment 61 might be used for the preparation of oxygen, none are so suitable as the mixture of manganese dioxide with potassium chlorate used in Experiment 20. The effect of adding the manganese dioxide to the potassium chlorate is to lower the temperature at which the gas comes off, and thus to prevent fusion. It will be shown (Experiment 62) that the manganese dioxide does not undergo any chemical change in the process nor suffer any loss of weight, that is to say it does not give up any of its own oxygen. It simply helps the potassium chlorate to part with its oxygen. There are many examples of this sort of action in chemistry; they are called catalytic actions, and the agents which bring them about are called catalysts. We can therefore write the equation for the reaction, leaving out of account the manganese dioxide altogether:

$$2KClO_3 = 2KCl + 3O_2.$$

EXPERIMENT 62.

The Catalytic action of Manganese Dioxide.

To a few grams of finely powdered potassium chlorate add about half its bulk of carefully weighed manganese dioxide. Heat in a hard glass tube for some time. Allow to cool, then boil up with distilled water and filter through a weighed filter paper. Repeat the boiling with fresh quantities of distilled water until all the solid has been removed from the tube to the weighed filter. Wash the solid on the filter with several quantities of boiling distilled water, so as to ensure that all potassium chlorate and chloride (which are both soluble) are washed through. Dry the filter paper in a steam-oven and weigh.

You will find the weight of the manganese dioxide the same as before, showing that its action was catalytic.

The laboratory method of preparation of oxygen is not used on the large scale for the commercial preparation of oxygen. There is a considerable demand for the gas, mainly for use in the oxy-acetylene blowpipe for cutting and welding metals, but also in cases of pneumonia and in aviation to assist breathing (see Chapter IX). The only method now used for the preparation of oxygen on a large scale is the liquefaction and subsequent evaporation of air. Since air is a mixture of oxygen (boiling-point $-182{\cdot}5°$ C.) and nitrogen (boiling-point $-194°$ C.) it will separate into these two gases when it is liquefied and allowed to evaporate. As the liquid air rises in temperature, the nitrogen comes off first and then the oxygen. In practice elaborate devices are used for preventing loss of the oxygen.

ℭ Physical Properties of Oxygen.

(1) Colourless.
(2) Tasteless.
(3) Very slightly soluble in water; but it must be remembered that it is sufficiently soluble for fishes to breathe the dissolved oxygen without using the oxygen of the air.
(4) Heavier than air.
(5) Hard to liquefy.

ℭ Chemical Properties of Oxygen.

(1) Neutral to litmus.
(2) Does not burn.
(3) An excellent supporter of combustion, as it combines readily with a large number of metals and non-metals forming oxides.

ℭ Test for Oxygen.

It rekindles a glowing splinter of wood.

EXPERIMENT 63.

Heat some manganese dioxide with strong sulphuric acid in a test-tube and test for oxygen. [Be particularly careful with hot strong sulphuric acid.]

We have already (Chapter VIII) given a brief account of three classes of oxide, acid, basic, and neutral. We must now mention another class, the peroxides. These are oxides of metals containing more oxygen than the basic oxide. Basic oxides do not (with the exception of those of mercury, silver, platinum, and gold) give up their oxygen when they are heated, but peroxides do, and they also give it up if they are heated with strong sulphuric acid. As we have already seen (Experiment 50) they liberate chlorine from strong hydrochloric acid. (This reaction is common to many substances containing a high percentage of loosely-bound oxygen.)

Examples of peroxides are barium peroxide, lead peroxide, and manganese dioxide. Certain oxides of non-metals are also sometimes called peroxides, but are better called 'dioxides'.

Many substances besides peroxides, containing a large amount of oxygen, give up some of it on heating, and if this oxygen is taken up by some other substance, the substance is said to be oxidized. The substance with the high proportion of oxygen is called an oxidizing agent. For instance, if we burn magnesium in air, it becomes oxidized to magnesium oxide, and the oxidizing agent is the oxygen of the air. Or if we pass hydrogen over heated copper oxide, the hydrogen becomes oxidized to hydrogen oxide (water), and the oxidizing agent is the copper oxide. The following is a list of a few oxidizing agents:

strong sulphuric acid. peroxides.
nitric acid and nitrates.
chlorates, permanganates, bichromates.

EXPERIMENT 64.

Heat some nitre in a round-bottomed flask until it melts. Drop in a piece of red-hot charcoal, and note that it burns brightly, being oxidized by the nitre to carbon dioxide.

The term oxidation has, however, a wider application than simply 'putting oxygen in' to a substance. It may also mean making an addition of any non-metallic element to another element or compound. Thus if we make lead chloride from lead we say that the lead is oxidized, and if we make ferric chloride from ferrous we say that the ferrous chloride has been oxidized, because ferric chloride contains a greater proportion of chlorine (the non-metal part) than ferrous chloride.

We may, of course, increase the non-metal part by decreasing the metallic part. Thus if we remove the hydrogen from hydrochloric acid and set free the chlorine, we say that the hydrochloric acid has been oxidized.

The opposite action to oxidation is reduction, which has already been referred to (Experiment 46 (*b*)), and these two actions *always take place simultaneously*. For example, in passing hydrogen over copper oxide the copper oxide oxidizes the hydrogen to water, but is itself reduced to copper. Reduction consists in the addition of a metal or hydrogen to an element or compound; the same result is obtained when we bring about a diminution in the proportion of non-metal in a compound, as when copper oxide becomes copper.

Some common reducing agents are: hydrogen, coal-gas, carbon, sulphuretted hydrogen, sulphur dioxide in water, i. e. sulphurous acid, ferrous sulphate. It is convenient to have tests by which we can recognize an oxidizing and a reducing agent.

ℂ Soluble oxidizing agents liberate iodine from potassium iodide solution.

Iodine has a greyish-black colour, and when heated yields a violet vapour, so that it is easily recognized. If only a very small quantity of iodine is liberated, use can be made of the fact that even the smallest trace of iodine will give a deep blue colour with starch solution. The oxidizing agent removes the 'positive' or metallic constituent (the potassium) from potassium iodide, and turns it into its oxide, which forms potassium hydrate with the water. This would react with the liberated iodine. It is therefore necessary to have acid (usually dilute sulphuric acid) present to react with the potassium hydrate (forming potassium sulphate with it) or else the iodine will not be visible.

Apply the above test to all the oxidizing agents you can think of. Notice that insoluble oxidizing agents (such as copper oxide) do not respond to the test.

ℂ A soluble reducing agent decolorizes potassium permanganate solution acidified with sulphuric acid.

The reduction consists in removing the oxygen from the permanganate. Potassium permanganate is, as its name implies, a salt derived from permanganic acid, which is a compound of water with an oxide of manganese (Mn_2O_7) very rich in oxygen. When reduced this oxide loses most of its oxygen to the reducing agent and becomes MnO, which dissolves in the acid present (being a basic oxide) to form a colourless salt of manganese (manganese sulphate).

Apply this test to all the reducing agents you know. Does hydrogen answer the test? Why not?

We may now conveniently revise the properties of hydrogen.

ℂ Physical Properties of Hydrogen.

(1) Colourless.
(2) No smell.
(3) Lightest substance known.
(4) Insoluble in water.
(5) Hard to liquefy.

ℂ Chemical Properties of Hydrogen.

(1) Burns with a very hot, pale flame forming water,

$$2H_2 + O_2 = 2H_2O.$$

(2) Neutral to litmus (as distinguished from hydrogen ion which turns litmus red).

(3) Powerful reducing agent, converting metallic oxides into metals:

$$CuO + H_2 = H_2O + Cu.$$

This is because of the great affinity it has for oxygen.

ℂ Uses of Hydrogen.

The gas suggests itself at once as being suitable for filling balloons and airships. Its disadvantage for this purpose is its great inflammability. Helium, a gas which is somewhat heavier, but does not burn, is replacing hydrogen for this purpose.

The gas is also used for hardening fats, i.e. for converting an oil into a solid fat. This process is used in making margarine.

Hydrogen and oxygen together are used in the oxy-hydrogen blowpipe flame.

EXAMPLES ON CHAPTER XX.

1 From the equation

$$2KClO_3 = 2KCl + 3O_2,$$

calculate the volume of oxygen which you would obtain at N.T.P. by heating 1 gm. of potassium chlorate until all the oxygen was driven off.

2 From the equations

$$Zn + 2HCl = ZnCl_2 + H_2,$$
$$Mg + 2HCl = MgCl_2 + H_2,$$
$$3Fe + 4H_2O = Fe_3O_4 + 4H_2,$$

calculate the volume of hydrogen liberated by 1 gm. of each of the three metals, zinc, magnesium, and iron.

[Atomic weights, p. 229].

XXI

SULPHUR AND SULPHURETTED HYDROGEN

The element sulphur was known to the Romans because free sulphur is found in large quantities in Sicily. Much sulphur is still obtained from there, and after purification by distillation and condensation of the vapour, it is cast into sticks called roll sulphur; its vapour may be condensed to form a fine powder called ‘flowers of sulphur’. From roll sulphur we may obtain different forms of sulphur.

Experiment 65.

(*a*) Dissolve some roll sulphur in carbon disulphide (Care !), and leave the solution to evaporate (compare Experiment 7 (*a*)). Crystals of rhombic sulphur are produced.

(*b*) Melt some roll sulphur in an enamel mug, allow it to cool, make two holes in the crust which forms on the top, and pour out the remaining liquid sulphur. After cooling, break out the crust left in the mug; a mass of interlacing needle-shaped crystals will be found. This is called prismatic sulphur.

(*c*) Boil some roll sulphur in a large test-tube and pour the boiling liquid into cold water. A substance resembling india-rubber, called plastic sulphur, is obtained. Note that when it is handled it very soon loses its elasticity.

(*d*) Shake up some flowers of sulphur with carbon disulphide. The greater part dissolves, but an insoluble pale-coloured residue called amorphous sulphur (i. e. without crystalline shape) is left. We thus distinguish four forms of sulphur: rhombic, prismatic, plastic, and amorphous. We call these the allotropic forms of sulphur. We know that these allotropic forms are nothing but the element sulphur because 1 gm. of each form, when burnt and turned into sulphur oxide, gives the same mass of sulphur oxide and *nothing else.* Certain other elements, notably carbon and phosphorus, also have allotropic forms. Rhombic sulphur is the form which is stable at ordinary temperatures, and both prismatic and plastic sulphur soon change back into it. This explains why prismatic sulphur becomes opaque and plastic sulphur brittle on standing. Rhombic and prismatic sulphur are both soluble in carbon disulphide, but plastic and amorphous sulphur are insoluble. Sulphur in all its forms is insoluble in water. The effect of heat on sulphur is sufficiently striking to merit special notice. If roll sulphur is carefully melted without overheating it can be converted to a mobile straw-coloured liquid. On further heating this liquid darkens till it becomes nearly black, and so viscous that it will scarcely flow out of the vessel. As the temperature is still further raised it once more becomes mobile and finally boils at 448° C., giving off a dark brown vapour.

ℂ Chemical Properties of Sulphur.

(1) It burns with a blue flame, combining readily with oxygen to form sulphur dioxide with traces of sulphur trioxide. The main action may be represented thus:

$$S + O_2 = SO_2.$$

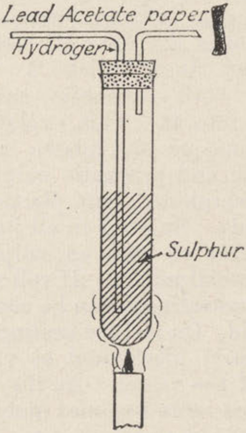
(2) It combines with chlorine, forming the evil-smelling sulphur chloride.

(3) It combines readily with many metals on heating, forming sulphides (see Experiment 14 in which iron sulphide was made):

$$Fe + S = FeS.$$

(4) It combines with hydrogen to form sulphuretted hydrogen.

This can be demonstrated by passing a stream of hydrogen through molten sulphur as shown. The issuing gas turns lead acetate paper black. This is a test for sulphuretted hydrogen (see below).



Note that sulphuretted hydrogen is decomposed by sparks or by heating into sulphur and hydrogen. The reaction between sulphur and hydrogen is therefore a balanced action, and we write it thus:

$$H_2 + S \rightleftarrows H_2S.$$

ℂ Preparation of Sulphuretted Hydrogen.

For use in the laboratory the gas is usually prepared in a Kipp's apparatus by the action of fairly strong hydrochloric acid on iron sulphide:

$$FeS + 2HCl = FeCl_2 + H_2S.$$

(This reaction was noted in Experiment 14.)

The gas is washed free from acid by passing it through water, and, if required dry, it must be passed through tubes containing phosphorus pentoxide, since it reacts both with strong sulphuric acid, calcium chloride, and quicklime.

The gas obtained from iron sulphide always contains some hydrogen, as the sulphide always contains some uncombined iron. A purer gas can be produced by substituting antimony sulphide for iron sulphide.

EXPERIMENT 66.

Collect some jars of sulphuretted hydrogen at the Kipp, and also make some sulphuretted hydrogen solution. Perform the following experiments (those marked * are performed with the solution):

(1) Pour litmus solution into a jar.
(2) Place pieces of metal foil in jars of the gas.
(3) *Add the solution to solutions of copper sulphate, lead acetate, antimony chloride.
(4) Apply a light to a jar of the gas.
(5) *Add the solution to acidified potassium permanganate.
(6) *Add strong nitric acid to the solution.
(7) Place a jar of chlorine in contact with a jar of moist sulphuretted hydrogen and allow the gases to mix.

ℂ Physical Properties of Sulphuretted Hydrogen.

(1) Colourless gas.
(2) Smell of bad eggs.
(3) Fairly soluble in water.
(4) Heavier than air.
(5) Hard to liquefy.
This gas is poisonous.

ℂ Chemical Properties of Sulphuretted Hydrogen.

(1) Its solution in water is a very weak acid, i. e. only a small proportion of its molecules is ionized. It forms two sets of salts called the normal and acid sulphides.

The normal sulphides are those in which both the hydrogen atoms of the sulphuretted hydrogen molecule are replaced by metal as in sodium sulphide, Na_2S, or iron sulphide, FeS. The acid sulphides are those in which only one of the hydrogen atoms of the sulphuretted hydrogen molecule is replaced by metal, as in acid sodium sulphide, $NaHS$.

We have already come across an acid forming two sets of salts in carbonic acid, H_2CO_3. ($H_2O + CO_2 = H_2CO_3$, see Chapter X.) For instance, the two carbonates of sodium are Na_2CO_3, normal sodium carbonate, and $NaHCO_3$, acid sodium carbonate, often called sodium bicarbonate. (The acid salts are often distinguished by the prefix 'bi'.)

We may classify acids according to the number of replaceable hydrogen atoms they contain per molecule, which we call their **basicity.**

Thus HCl (hydrochloric acid) and HNO_3 (nitric acid) are monobasic.

H_2SO_4 (sulphuric acid) and H_2CO_3 are dibasic.

H_3PO_4 (phosphoric acid) is tribasic, and can thus form *three* sets of salts:

Na_3PO_4, normal sodium phosphate.
Na_2HPO_4, disodium hydrogen phosphate.
and NaH_2PO_4, sodium dihydrogen phosphate.

All the hydrogen atoms of an acid are not necessarily replaceable by metallic atoms. Thus acetic acid has four hydrogen atoms in the molecular formula, but of these only one is replaceable, and it is therefore a monobasic acid.

A normal salt is thus a salt in which all the replaceable hydrogen of an acid has been replaced by metal, and an acid salt one in which only a part of the replaceable hydrogen of the acid has been replaced.

Many metals are attacked by sulphuretted hydrogen at ordinary temperatures, becoming covered with films of sulphide, e. g.

$$2Ag + H_2S = Ag_2S + H_2.$$

This action is the main cause of the tarnish which forms on metals when they are exposed to air, especially in towns, since the fumes of burnt coal-gas and from factory chimneys often contain sulphuretted hydrogen.

A number of metals have insoluble sulphides which are thrown down as precipitates when sulphuretted hydrogen is added to a solution containing the metallic ion, e. g.

$$CuSO_4 + H_2S = CuS + H_2SO_4.$$

The explanation of this action is that whenever a molecule of the insoluble sulphide is formed by the union of metal and sulphide ions it comes out of solution, and is therefore not re-ionized, but precipitated.

These sulphides are frequently highly coloured, and their formation is therefore often used as a test for the presence of the metallic ion.

Thus sulphuretted hydrogen sent into a solution containing copper ion or lead ion gives a black precipitate and into a solution containing antimony ion an orange precipitate. The action with lead is often used as a test for sulphuretted hydrogen, as extremely small quantities of the gas will cause the formation of the insoluble lead sulphide. Lead acetate is chosen as being a convenient soluble salt of lead.

(2) It burns with a blue flame, forming sulphur if the supply of air is limited, and sulphur dioxide in a plentiful supply of air.

$$2H_2S + O_2 = 2H_2O + 2S.$$
$$2H_2S + 3O_2 = 2H_2O + 2SO_2.$$

It is a non-supporter of combustion.

(3) It is a reducing agent, and therefore decolorizes acid potassium permanganate. It also reacts with a large number of oxidizing agents which oxidize it to sulphur (see Chapter XX: here taking hydrogen out of the molecule constitutes the oxidation). The general equation representing the reaction is $2H_2S + O_2 = 2H_2O + 2S$. Nitric and strong sulphuric acids act on it in this way. The reaction with chlorine is similar: $H_2S + Cl_2 = 2HCl + S$. This is another example of the great affinity of chlorine for hydrogen.

¶ Volume Composition and Formula.

If a spiral of copper wire be enclosed in a volume of the gas contained in a piece of tubing sealed at both ends, and heated, the metal decomposes the gas, forming copper sulphide and liberating hydrogen. On cooling and opening the tube under water the volume of gas is found to be unchanged. Therefore one volume of the gas yields one volume of hydrogen, and hence, by Avogadro's Law, one molecule of the gas contains one molecule of hydrogen. Thus the formula of the gas is H_2S_x.

But the vapour density of the gas is 17. (See page 116.)

Therefore its Molecular Weight is 34.

Therefore the weight of sulphur in the molecule is

$$(34-2)=32.$$

But this is the weight of one atom of sulphur.

Therefore there is one atom of sulphur in the molecule.

Therefore the Molecular Formula is H_2S.

Compare this reasoning carefully with that used in finding the formula for water and for hydrochloric acid. (See pp. 99 and 114.) The difference arises from the fact that in this case the substances concerned are not all gaseous. We cannot assume anything about the volume of the sulphur because it is a solid.

EXAMPLES ON CHAPTER XXI.

1 Calculate the percentage composition of silver sulphide, Ag_2S, from the formula.

2 Write down all the meanings of the equation

$$2H_2S+3O_2=2H_2O+2SO_2.$$

3 What volume of sulphuretted hydrogen at N.T.P. can be obtained from 10 gm. of ferrous sulphide, FeS, by the action of acid ?

XXII

SULPHUR DIOXIDE, SULPHUR TRIOXIDE, AND SULPHURIC ACID

Experiment 67.

Preparation of Sulphur Dioxide.

Use the same apparatus as in Experiment 51. Place a very small quantity of copper turnings in the flask, and add enough strong sulphuric acid to cover them. Heat until the reaction starts, and then remove the flame. Collect by downward displacement about four jars, and pass the remaining gas into water. Preserve the residue in the flask.

Perform the following tests with the gas :

(1) Pour in litmus solution.

(2) Plunge in a lighted taper.

(3) Place a jar mouth to mouth with a jar of moist sulphuretted hydrogen.

(4) Add a solution of the gas to acidified potassium permanganate solution.

¶ Explanation of the action of strong Sulphuric Acid on Copper.

You found in Experiment 15 that dilute sulphuric acid has no effect on copper, i.e. no hydrogen is liberated from the acid as would be the case if magnesium or zinc were used. The strong acid, however, acts when hot, and its action here is an oxidizing action, to convert the copper to copper oxide which dissolves in excess of the acid forming copper sulphate, and to be itself reduced to sulphurous acid. We already know that copper is a reducing agent since it tends to take up oxygen from the air and form copper oxide. (Experiment 46 (*b*).)

We can most profitably study the properties of sulphur dioxide by comparing them with the corresponding properties of carbon dioxide as in the following table:

Carbon Dioxide.	*Sulphur Dioxide.*
Physical Properties.	
Colourless.	Colourless.
Faint pungent smell.	Choking smell.
Fairly soluble.	More soluble than carbon dioxide.
Heavier than air.	Heavier than air.
Easy to liquefy.	Easier to liquefy than carbon dioxide.

Chemical Properties.

Carbon Dioxide.	*Sulphur Dioxide.*
The aqueous solution contains the acid carbonic acid and reddens litmus.	The aqueous solution contains the acid sulphurous acid and reddens litmus.
This acid is dibasic, and forms normal and acid carbonates.	This acid is dibasic, and forms normal and acid sulphites.
The gas does not burn, nor does it support ordinary combustion, but magnesium will burn in it.	Ditto.
The gas reacts with lime-water, forming a white precipitate of calcium carbonate: $CO_2 + Ca(OH)_2 = CaCO_3 + H_2O$.	The gas reacts with lime-water, forming a white precipitate of calcium sulphite: $SO_2 + Ca(OH)_2 = CaSO_3 + H_2O$.
This precipitate is soluble if excess of carbon dioxide is sent in as it becomes converted to the soluble bicarbonate: $CaCO_3 + CO_2 + H_2O = Ca(HCO_3)_2$.	This precipitate is soluble if excess of sulphur dioxide is sent in as it becomes converted to the soluble bisulphite: $CaSO_3 + SO_2 + H_2O = Ca(HSO_3)_2$.
Reacts with caustic soda and caustic potash in a similar way, forming the carbonate or acid carbonate.	Reacts with caustic soda and caustic potash in a similar way, forming the sulphite or acid sulphite.
Carbonic acid, the solution of carbon dioxide in water, is not a reducing agent.	Sulphurous acid, the solution of sulphur dioxide in water, is a reducing agent because it tends to form sulphuric acid: it will therefore decolorize potassium permanganate.
Carbonic acid is not a bleaching agent.	Sulphurous acid is a bleaching agent, but, unlike chlorine, it bleaches by reduction and not by oxidation.

Carbon Dioxide.	*Sulphur Dioxide.*
Methods of Preparation.	
Burn carbon in air or oxygen.	Burn sulphur in air or oxygen.
Heat a carbonate (not of sodium or potassium) or a bicarbonate.	Heat a sulphite (not of sodium or potassium) or a bisulphite.
*Treat a carbonate or bicarbonate with dilute acid.	Treat a sulphite or bisulphite with dilute acid.
Oxidize the lower oxide: $2CO + O_2 = 2CO_2$.	Reduce the higher oxide: $2SO_3 - O_2 = 2SO_2$.
CO is carbon monoxide.	*(In particular the reduction of sulphuric acid by copper.)

NOTE.—The preparations marked * are the ones used in the laboratory.

Uses.

The applications of carbon dioxide in industry have already been discussed (Chapter IX). The most important uses of sulphur dioxide are as follows:

(1) For the manufacture of sulphuric acid (see below).

(2) For bleaching delicate materials such as silks, woollens, and sponges which would be damaged by chlorine.

(3) As a disinfectant: but for this purpose it is being superseded by more convenient substances such as formalin.

(4) For creating low temperatures: by the evaporation of liquid sulphur dioxide a temperature of about −50° C. can be obtained.

ℭ Volume Composition and Formula.

Exactly the same method is used in finding the volume composition and formula for the two gases. A piece of sulphur is confined over mercury in a volume of oxygen as shown in Experiment 34. It is ignited by heating a fine platinum wire in contact with it electrically. When it has finished burning the volume of the gas is found to be unchanged. We may therefore say that

1 volume of sulphur dioxide contains 1 molecule of oxygen.

Therefore, by Avogadro's Law,

1 molecule of sulphur dioxide contains 1 molecule of oxygen.

Therefore the molecular formula is S_xO_2.

But the Vapour Density is 32.

Therefore the molecular weight is 64.

But the weight of oxygen in the molecule is 32.

Therefore the weight of sulphur is 32.

But one atom of sulphur weighs 32.

Therefore there is one atom of sulphur in the molecule.

Therefore the molecular formula is SO_2.

Similarly the molecular formula of carbon dioxide is CO_2.

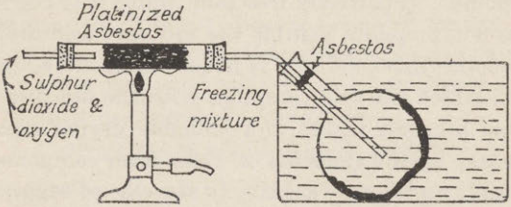
Sulphur dioxide cannot combine directly with free oxygen except in the presence of a catalyst, such as platinized asbestos, and under certain conditions of temperature and pressure. It then forms a white solid, sulphur trioxide, having the formula SO_3.

EXPERIMENT 68.

Demonstration.

Preparation of Sulphur Trioxide.

Prepare some platinized asbestos by soaking asbestos wool in a strong solution of hydrochloroplatinic acid and heating strongly in an evaporating dish. The acid is decomposed by heat, and finely divided platinum deposited on the asbestos. Pack the asbestos into a hard glass tube, pass oxygen and sulphur dioxide through it, and heat. Collect the sulphur trioxide in a well-cooled flask.



Note that the gases, tubes, flask, &c., must be perfectly dry.

Add water to the sulphur trioxide ; note the violent action. Test with litmus, and note that the solution is acid, and also gives a white precipitate with barium chloride solution.

When sulphur trioxide combines with water sulphuric acid is produced.

$$H_2O + SO_3 = H_2SO_4.$$

This process of making sulphuric acid is used on a large scale, and is called the 'Contact Process'. There is no simple laboratory method of preparing the acid since it is non-volatile, and cannot therefore be liberated from its salts in the same way as nitric or hydrochloric acids.

EXPERIMENT 69.

Pour some strong sulphuric acid into water very cautiously, and note the great rise of temperature.

Pour some strong sulphuric acid into potassium iodide solution and into sulphuretted hydrogen solution.

Pour strong sulphuric acid into a beaker containing about 50 c.c. of hot strong sugar solution. The beaker should be stood in the sink.

Strong sulphuric acid is a heavy oily liquid with a high boiling-point. If perfectly free from water it is not ionized, and does not therefore exhibit the ordinary acid properties, but in practice this condition is never obtained owing to the ease with which the acid combines with the moisture of the air. This property makes it a valuable drying agent. It can also take up the elements of water from compounds like sugar, oxalic and formic acids. In the case of sugar, as you have seen, a black mass of carbon is left. The action with the acids will be considered later under carbon monoxide. Its very corrosive action on the skin is due to the fact that it withdraws water from it. The strong acid is also a good oxidizing agent, and therefore liberates iodine from potassium iodide, and oxidizes sulphuretted hydrogen to sulphur. It also oxidizes many metals (e. g. copper, Experiment 67) to their sulphates, being reduced by them at the same time to sulphur dioxide.

The strong acid liberates volatile acids from their salts owing to the fact that it is non-volatile itself (see Chapter XVIII).

The dilute acid has none of these properties, but has the ordinary properties of a strong acid (see Chapter XVIII). It is not, however, such a strong acid as hydrochloric acid, as it is not so highly ionized. It is a dibasic acid, forming both normal and acid sulphates.

EXPERIMENT 70.

Preparation of Normal and Acid Sodium Sulphates.

Place 25 c.c. of bench caustic soda in an evaporating dish, add a few drops of litmus, and run in bench dilute sulphuric acid from a burette until the colour of the litmus just changes. Read the volume of acid used, and run the same quantity into a fresh lot of 25 c.c. of caustic soda in an evaporating dish without litmus, since we do not want a coloured product this time. Concentrate slightly by evaporating on a water bath, and pour into a crystallizing dish.

The reaction is expressed as follows:

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O.$$

Make crystals also by adding to the same quantity of caustic soda a double volume of the acid, when acid sodium sulphate is formed in accordance with the equation:

$$2NaOH + 2H_2SO_4 = 2NaHSO_4 + 2H_2O.$$

You will easily be able to distinguish between the long-shaped crystals of the normal sulphate and the tabular crystals of the acid sulphate. The latter are more slow in crystallizing than the former.

ℂ Preparation of Sulphates.

(1) Dissolve the metal in sulphuric acid.

EXPERIMENT 71.

Preparation of Copper and Iron Sulphates.

Pour the residue in the flask from Experiment 67 into a small quantity of water. Filter, and concentrate the filtrate by evaporation until crystals form. These consist of blue vitriol (copper sulphate), $CuSO_4 . 5H_2O$.

The action is as follows:

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$

The black part of the residue consists partly of copper oxide and partly of copper sulphide, some of which is always formed in this reaction. This is not shown in the equation.

To 30 or 40 c.c. of sulphuric acid (1 vol. acid to 10 vols. of water) in a large evaporating dish add iron filings in small quantities until no further reaction takes place, heating gently all the time. Pour boiling water several times through a funnel, and filter hot. The filtrate must not be concentrated or the crystals will be decomposed, since they are readily oxidized by air. Beautiful green crystals of green vitriol (ferrous sulphate) are formed, having the formula $FeSO_4 . 7H_2O$. The action is as follows:

$$Fe + H_2SO_4 = FeSO_4 + H_2.$$

Note: The old-fashioned name for sulphuric acid was 'Oil of Vitriol', and several of the common sulphates were therefore called 'vitriols'.

(2) Dissolve the oxide, hydroxide, or carbonate in sulphuric acid.

This was the method used in Experiment 70.

(3) Precipitate an insoluble sulphate.

The commoner insoluble sulphates are those of barium, lead, strontium, and calcium, of which barium is much the most insoluble. The formation of a white precipitate of barium sulphate which is insoluble in nitric or hydrochloric acids is used as a test for sulphate ion. (Experiment 68.)

EXAMPLES ON CHAPTER XXII.

1 Find the percentage composition of sulphuric acid from the formula H_2SO_4.

2 From the equation

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O,$$

find out what weight of caustic soda is required to produce 20 gm. of sodium sulphate.

XXIII

ACIDIMETRY AND ALKALIMETRY

A standard solution is one which contains a known weight of the dissolved substance per c.c. By the use of such solutions we may make a variety of quantitative determinations much more quickly and easily than in any other way. We shall here discuss their use in finding the strengths of solutions of acids (acidimetry) and alkalies (alkalimetry).

A normal solution of an acid is one which contains 1 gm. of replaceable hydrogen per litre. In the case of a monobasic acid, the normal solution will therefore contain the molecular weight per litre, in the case of a dibasic acid, half the molecular weight, for a tribasic acid, one third, and so on.

Thus:

Hydrochloric acid, HCl, is monobasic.
Molecular weight $= 1 + 35{\cdot}5 = 36{\cdot}5$.
Normal solution contains 36·5 gm. per litre.
Sulphuric acid, H_2SO_4, is dibasic.
Molecular weight $= 2 + 32 + 64 = 98$.
Normal solution contains $\frac{98}{2} = 49$ gm. per litre.
Phosphoric acid, H_3PO_4, is tribasic.
Molecular weight $= 3 + 31 + 64 = 98$.
Normal solution contains $\frac{98}{3} = 32{\cdot}7$ gm. per litre.

Of the three common acids, hydrochloric, sulphuric, and nitric, not one can be weighed out exactly without very great trouble. If we want to make a standard solution of an acid by weighing we therefore choose oxalic acid, which is a white crystalline solid, and easily obtained pure. Its formula is $C_2O_4H_2 \,.\, 2H_2O$, and it is dibasic. Its molecular weight being 126, a normal solution will contain 63 gm. per litre.

EXPERIMENT 72.

Preparation of Normal Oxalic Acid Solution.

Weigh out accurately on to a watch-glass 6·3 gm. of the finely powdered crystalline acid. Transfer the acid to a beaker with the aid of a wash-bottle, taking great care to avoid any loss, and add enough distilled water to dissolve the crystals. Warm gently if necessary. Pour the solution carefully into a 100 c.c. measuring flask, taking great care to avoid loss, and rinsing the beaker with a small quantity of water into the flask. Add distilled water up to the mark and shake well. Note that this operation must be done when the solution in the flask is at the temperature of the room. Transfer the solution to a stoppered bottle and label.

A normal solution of a base is one which contains 17 gm. of hydroxyl, i. e. one hydroxyl group, OH, per litre. Equal volumes of normal acids and bases will therefore react together to form water and a salt, because the hydrogen and hydroxyl have been added in the right proportions. We have already (Experiment 27) shown how we can use litmus to show when equivalent quantities of acid and alkali have been added to each other. Many other substances may be used in the same way, and are called 'indicators'. Two which are commonly used are phenol phthalein and methyl orange. Indicators change their colour according as the number of hydrogen ions in the solution in which they are put is greater than, equal to, or less than the number of the hydroxyl ions, i. e. according as the solution is acid, neutral, or alkaline. In acid solution phenol phthalein is colourless and methyl orange is red, and in alkaline solution phenol phthalein is red and methyl orange is yellow. These indicators are not necessarily all equally suitable for the same experiment, but at this stage the student will be told in each case which is the best indicator to use.

EXPERIMENT 73.

Preparation of Decinormal Oxalic Acid Solution.

Suck up 25 c.c. of normal oxalic acid into a pipette with care, remembering it is poisonous, and run the acid into a 250 c.c. measuring flask. Make up to the mark with distilled water and mix by shaking well.

EXPERIMENT 74.

Preparation of Decinormal Caustic Soda Solution.

Caustic soda cannot be weighed out accurately since it is deliquescent. A normal solution will contain 40 gm. per litre ($NaOH = 23 + 16 + 1 = 40$), and hence 300 c.c. of decinormal will contain 1·2 gm. 1·5 gm. of the solid are therefore quickly and roughly weighed out and placed in a stoppered bottle to which 300 c.c. of distilled water are added. Air must be excluded as far as possible from solutions of caustic soda and caustic potash, since these substances react with the carbon dioxide present in it. When the caustic soda has dissolved, shake well, rinse out a burette with some of the solution, and then fill it with the solution. By means of a pipette run 25 c.c. of $N/10$ oxalic acid into a conical flask. Add a few drops of phenol phthalein solution and run in the caustic soda solution slowly from the burette until the red colour just appears. Repeat several times and take the mean of the volume of alkali required to neutralize 25 c.c. of the acid. This process is called titration. Record as shown in Experiment 27.

Since equal volumes of solutions of equal strengths react together, the strengths of two solutions will be inversely proportional to the volumes of the two solutions reacting together.

Thus suppose in the above experiment, 25 c.c. of the oxalic acid are found to react with 20 c.c. of the caustic soda solution of unknown strength X, then we may say:

$$\frac{X}{N/10} = \frac{25}{20},$$

whence $$X = N/10 \times \frac{25}{20},$$

or $$X = N \times 0{\cdot}125.$$

This solution must now be diluted until it is of exactly decinormal strength.

1 c.c. of this alkali contains $\frac{40 \times 0{\cdot}125}{1000}$ gm. alkali,

but 1 c.c. of required alkali contains $\frac{40 \times 0{\cdot}1}{1000}$ gm. alkali,

$\therefore$ $\frac{0{\cdot}1}{0{\cdot}125}$ c.c. of this alkali will make 1 c.c. of the required alkali,

$\therefore$ $\frac{250 \times 0{\cdot}1}{0{\cdot}125}$ c.c. of this alkali will make 250 c.c. of the required alkali.

This volume of alkali is therefore measured out into a 250 c.c. measuring flask, and distilled water added up to the mark. Transfer to a stoppered bottle and label.

EXPERIMENT 75.

Preparation of Decinormal Hydrochloric Acid.

Place 3 c.c. of concentrated hydrochloric acid in a 250 c.c. flask, and fill up to the mark with distilled water and mix well. This solution will now be about the right strength. Titrate against *N*/10 caustic soda, using litmus as indicator, and running the alkali into the acid from the burette. Calculate the exact strength of the acid solution and make up 100 c.c. of exactly *N*/10 acid.

It is clear that we could use a volumetric method like the one in this experiment to prove that the amount of sulphuric acid in a water voltameter is unchanged by electrolysis. (See p. 28.)

EXPERIMENT 76.

Use of Sodium Carbonate as Standard Alkali.

Although sodium carbonate is a salt, its solution can be titrated against acid, since it gives an alkaline reaction with indicators. The equation representing the reaction with hydrochloric acid is:

$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2.$$

In order, therefore, that a normal solution of sodium carbonate shall react with an equal volume of a normal acid solution, the normal sodium carbonate must contain half its molecular weight per litre, that is, 53 gm.

Since pure anhydrous sodium carbonate can be obtained, this gives us a means of making directly a standard solution of an alkali which we cannot do in the case of caustic potash or soda. Make up 100 c.c. of normal sodium carbonate.

EXPERIMENT 77.

To find the percentage purity of a sample of Oxalic Acid.

Assume the acid to be pure, and make up 100 c.c. of normal strength as in Experiment 72. Titrate against normal caustic soda, with phenol phthalein as indicator. Calculate as follows:

Suppose 25 c.c. of the normal alkali reacted with 26 c.c. of the acid solution.

Then the strength of the acid is $N \times \frac{25}{26}$.

Therefore the percentage purity of the acid is

$$\frac{25}{26} \times 100 = 96{\cdot}15 \text{ per cent.}$$

EXAMPLES ON CHAPTER XXIII.

1 Write down the weight of
  (*a*) Sulphuric acid required to make 1 litre of normal acid.
  (*b*) Hydrochloric acid required to make 1 litre of decinormal acid.
  (*c*) Nitric acid required to make 1 litre of 2 × normal acid.

2 21·5 c.c. of N acid was equivalent to 25 c.c. of caustic soda solution of unknown strength. Find the strength of the caustic soda
  (*a*) in normalities;
  (*b*) in grams per litre.

3 How much $N \times 1{\cdot}176$ acid is required to make 1 litre of N acid?

4 Find the percentage purity of a sample of oxalic acid from the following results:

The acid was assumed pure, and 6·3 gm. were made up to 100 c.c. The solution was titrated against normal caustic soda, when it was found that 26·5 c.c. of the acid solution were equivalent to 25 c.c. of the alkali.

XXIV

NITROGEN AND AMMONIA

(*a*) Nitrogen.

We have already (Chapter VII) referred to nitrogen as the gas which, together with oxygen, constitutes the main part of the atmosphere. A sample of moderately pure nitrogen is best obtained from the atmosphere by removing the oxygen from a closed volume of air by means of burning or smouldering phosphorus.

¶ Physical Properties.

(1) Colourless gas.
(2) No smell.
(3) Only slightly soluble in water.
(4) Lighter than air ; this you could have found out for yourself, since oxygen is heavier than air, and air is a mixture of the two gases.
(5) Hard to liquefy.

ℂ Chemical Properties.

The gas exhibits great lack of chemical activity, that is to say, that it will not readily combine with other elements. It does not even combine readily with oxygen, and therefore it will not burn, and since it does not readily combine with other elements it will not support combustion. It is supposed that the two atoms in the molecule of nitrogen are so firmly united to one another that they are only with difficulty separated and made to join up with other atoms.

ℂ The Importance of Nitrogen in Nature.

This element is one of the essential constituents of protoplasm, the living matter of which the cells of plants and animals are composed. All plants and animals must therefore take in nitrogen in some form, and the provision of a sufficient supply of the element in forms suited to this purpose is sometimes spoken of as the 'Nitrogen Problem'.

Carnivorous and herbivorous animals cannot make any use of the vast quantities of free nitrogen in the atmosphere. They can only assimilate the element when it is in the form of proteins, which are highly complex substances containing nitrogen as an essential constituent. The carnivorous animals derive their protein by eating the flesh of other animals, and the herbivorous animals get theirs from plants. Plants, unlike animals, require their nitrogen in a very simple form, either as nitrates or as ammonia compounds. (Ammonia is a compound of nitrogen and hydrogen.) They take these nitrogen compounds in from the soil through their roots.

In uncultivated country the nitrogen content of the soil does not vary greatly, as it is continually renewed by the decay of plants. When the dead plant-body falls into the soil it is attacked by soil bacteria, which convert its complex proteins into simple nitrogen compounds, which then serve to supply the next generation of plants with nitrogen. Other additions to the nitrogen compounds in the soil are also made (1) by rain bearing traces of nitric acid (see next chapter), and (2) by waste nitrogen products excreted by animals. In some cases this second contribution may be large, as on certain islands where sea-birds congregate and deposit a large quantity of excrement called 'guano'.

When the soil is cultivated the case is totally different, as in general the plant-bodies are removed, and there is thus no automatic renewal of the nitrogen content of the soil. Moreover, in order to make agriculture profitable the crops must be as heavy as possible, that is to say, the soil must have a plentiful supply of nitrogen compounds available for all the plants grown in it. This condition is brought about by adding natural or artificial manure, the latter consisting of nitrates of sodium or calcium or of ammonium sulphate.

Long before anything was known about the necessity of nitrogen for plant life it was found that it was very advantageous to alter the kind of crop grown year by year on any given piece of ground; for instance, if wheat had been grown one year, experience showed that it was desirable to grow peas or clover the next. This is spoken of as the rotation of crops. The explanation of this fact is very interesting: plants like peas, beans, clover, &c., have small swellings on their roots in which certain bacteria live in great numbers. These have the power of taking up the free nitrogen of the air, and building it up into proteins for the plant. Some of these proteins are attacked by the soil bacteria and converted into ammonia compounds, so that the total result of growing a crop of peas or beans is to enrich the soil very considerably as regards nitrogen.

(*b*) Ammonia.

When animal protein (e.g. horns and hoofs of cattle, &c.) is heated in absence of air the nitrogen is given off as ammonia. This was the way in which a solution of the gas was originally prepared, and it was therefore called 'Spirit of Hartshorn'. Since coal contains a certain amount of combined nitrogen owing to its formation from decaying vegetable matter, it also yields ammonia when it is heated in absence of air as in the manufacture of coal-gas. The distillation of coal is in fact at present the principal source of the ammonia of commerce in Great Britain. Most of this ammonia comes on the market as ammonium sulphate for use as artificial manure. In Germany ammonia is made by the direct union of nitrogen and hydrogen. These gases do not combine under ordinary conditions, but in the presence of a catalyst, such as finely divided iron, and under great pressure and at a low temperature combination occurs: $N_2 + 3H_2 = 2NH_3$. This is called Haber's Process, and we shall refer to it again in the next chapter.

In the laboratory ammonia is always prepared from its compounds. The most ready method of preparation is to warm some 0·880 ammonia solution (a saturated solution of the gas in water) in a flask provided with a cork, through which passes a fairly long straight tube. If a gas-jar is inverted over the end of this tube it is filled with the gas in a very short time. If the gas is required dry, it must be passed through a tower containing quicklime. Neither calcium chloride nor sulphuric acid can be used to dry ammonia, since it forms a compound with calcium chloride and ammonium sulphate with sulphuric acid.

EXPERIMENT 78.

The Properties of Ammonia.

Collect a few jars of the gas, and perform the following experiments :

(1) Remove the plate from a jar under water and note the extreme solubility of the gas. The 'fountain experiment' may be performed with it. (Experiment 54.)

(2) Note that its solution turns litmus blue: the solution in water must therefore contain hydroxyl ions.

(3) Note that the gas does not burn, nor does it support combustion. Careful observation will show that very close to the flame of the taper some of the gas is split up into nitrogen and hydrogen by the heat of the flame, and the hydrogen then burns. The gas can be made to burn in oxygen, when water is formed and nitrogen set free.

(4) Pour a little strong hydrochloric acid into a jar of the gas, and note the production of dense white fumes of ammonium chloride: $NH_3 + HCl = NH_4Cl$. (Compare Experiment 53.)

(5) Pour a little copper sulphate solution into a jar, and note the formation of pale-blue copper hydroxide which dissolves in excess of ammonia, giving an intense blue solution.

ℂ Physical Properties.

(1) Colourless gas.
(2) Very pungent smell.
(3) Very soluble in water.
(4) Lighter than air.
(5) Easily liquefied.

ℂ Chemical Properties: Ammonia and Ammonium.

(1) The most striking chemical property of ammonia gas, NH_3, is its reaction with water to form ammonium hydroxide, NH_4OH.

$$NH_3 + H_2O = NH_4OH.$$

We may compare this action with that of carbon dioxide and sulphur dioxide with water, forming carbonic and sulphurous acids respectively:

$$CO_2 + H_2O = H_2CO_3.$$
$$SO_2 + H_2O = H_2SO_3.$$

Ammonium hydroxide has the general properties of a base, and closely resembles sodium and potassium hydroxides.

EXPERIMENT 79.

Formation of an Ammonium Salt.

Pour 50 c.c. of bench ammonium hydrate into a measuring cylinder, add methyl orange, and pour in bench dilute sulphuric acid till the colour just changes (stir well). Note the volume of acid required. Repeat without indicator, pour into an evaporating dish, concentrate and crystallize. Crystals of ammonium sulphate are obtained:

$$H_2SO_4 + 2NH_4OH = (NH_4)_2SO_4 + 2H_2O.$$

Ammonium hydroxide forms salts with acids in exactly the same way that sodium and potassium hydroxides do. In these salts the group NH_4 takes the place of the metal sodium or potassium, just as it does in the hydroxide. We therefore call it a metallic radicle, and it is given the name ammonium. The ammonium salts resemble closely in appearance and properties the corresponding salts of potassium and sodium, but they usually differ from them in their behaviour on heating. This will be discussed fully in Chapter XXX.

We must distinguish clearly between ammonia, NH_3, a pungent gas, and ammonium, NH_4, a metallic radicle which has never been isolated, but exists in a number of compounds.

(2) Ammonia is a volatile substance, and is therefore liberated from ammonium compounds by non-volatile bases in exactly the same way as volatile acids are liberated from their salts by a non-volatile acid such as sulphuric. Thus if ammonium chloride or sulphate is heated in a dry tube with lime, caustic soda or soda lime (caustic soda and lime fused together), ammonia gas is given off, and the same thing happens if a solution of an ammonium salt is boiled with a solution of an alkali (Experiment 44). This fact is used to test for ammonium compounds, the gas being recognized by its smell. The first action of an alkali like sodium hydroxide on an ammonium salt is to produce ammonium hydroxide:

$$NH_4Cl + NaOH \rightleftharpoons NH_4OH + NaCl.$$

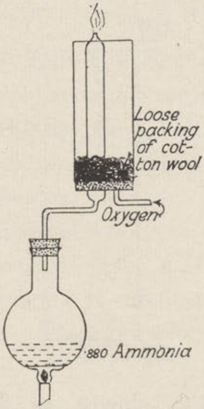
The ammonium hydroxide, however, readily splits up into ammonia (NH_3) and water (H_2O), so that the balanced action is upset and the reaction proceeds entirely from left to right.

(3) The gas does not burn in air nor will it support combustion, but it burns in oxygen.

EXPERIMENT 80.

Demonstration.

Cause a gentle stream of ammonia gas to pass through a piece of tubing of diameter about 4 cm. fitted into a lamp-glass as shown. Pass oxygen into the glass, and fill the lower part of the lamp-glass with a loose packing of cotton-wool, so as to spread the oxygen through the whole glass.



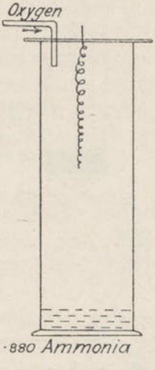
When the oxygen is turned on the ammonia can be ignited, and burns with a yellowish-brown flame. The true colour of the flame is best seen if a roll of platinum foil is placed inside the glass tube at the jet: if not, the yellow colour of the hot glass masks the colour of the ammonia flame.

EXPERIMENT 81.

Demonstration.

Oxidation of Ammonia.

Heat a spiral of platinum wire which passes through a piece of asbestos board, and support the board on the top of a gas-jar containing a few c.c. of 0·880 ammonia. The spiral will be seen to glow, and white fumes of ammonium nitrite (NH_4NO_2, ammonium nitrate being NH_4NO_3; cf. Na_2SO_3, sodium sulphite, and Na_2SO_4, sodium sulphate) are produced.



On passing in oxygen slowly, as shown, brown fumes of nitrogen dioxide are formed. If the oxygen is sent in somewhat rapidly the action will become violent, making the spiral red-hot, which then ignites the liberated hydrogen with explosion.

(4) The gas gives dense white fumes of ammonium chloride with hydrochloric acid.

(5) The gas gives an intense blue colour with compounds of copper.

EXPERIMENT 82.

Volume Composition of Ammonia.

Electrolysis of one volume of 0·880 ammonia with ten times its volume of a saturated sodium chloride solution in a voltameter shows that in this gas three volumes of hydrogen are combined with one volume of nitrogen.

The formula is therefore $(NH_3)_x$.

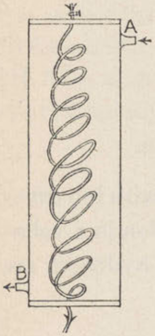
But the vapour density is 8·5.

Therefore the molecular weight is 17.

But the atomic weights of nitrogen and hydrogen are 14 and 1 respectively. Therefore $x = 1$, and the formula is NH_3.

ℂ Uses of Ammonia.

As already mentioned, a great deal of ammonia is converted into ammonium sulphate for manure. The gas is also largely used in refrigerators, advantage being taken of the fact that the liquefied gas takes up a great deal of heat from its surroundings when it evaporates. If the liquid ammonia is dropped through a stopcock into a spiral iron tube, placed in a vessel containing a solution of calcium chloride in water which does not freeze easily, it will evaporate in the coil, and, by taking up heat from its surroundings, will greatly lower the temperature of the solution. The cold solution then leaves the tank at B and circulates round vessels filled with water which is to be frozen, or round chambers containing foods to be kept in cold storage. The solution returns to the tank at A.



EXAMPLES ON CHAPTER XXIV.

1 Calculate the percentage of ammonia, NH_3, in :
  (*a*) ammonium chloride, NH_4Cl;
  (*b*) ammonium sulphate, $(NH_4)_2SO_4$.

2 What weight of slaked lime, $Ca(OH)_2$, will decompose 20 gm. of ammonium chloride?

$$Ca(OH)_2 + 2NH_4Cl = CaCl_2 + 2NH_3 + 2H_2O.$$

XXV

NITRIC ACID AND THE OXIDES OF NITROGEN

Experiment 83.

Preparation of Nitric Acid.

Place about 10 gm. of sodium nitrate in a glass-stoppered retort, and run in through a funnel enough strong sulphuric acid to cover the solid. Heat gently, and collect the nitric acid which distils over in a well-cooled receiver.

Refer to the explanation of this balanced action in Chapter XII.

The equation for the reaction is

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3,$$

the normal sulphate not being produced at the low temperature necessary to avoid decomposition of the nitric acid.

1. Test the specimen of acid you collect for acid properties with litmus and marble, and write an equation for the latter reaction.

2. Test the oxidizing powers of the acid.

(*a*) Boil some flowers of sulphur with the acid, dilute somewhat and filter. The filtrate will give a white precipitate of barium sulphate with barium chloride solution, showing that the sulphur has been oxidized to sulphuric acid thus:

$$2S + 3O_2 + 2H_2O = 2SO_3 + 2H_2O = 2H_2SO_4.$$

(*b*) Preparation of phosphoric acid. Place 25 gm. of red phosphorus in a large basin in a fume cupboard, and cover it with strong nitric acid diluted with its own volume of water. Heat the basin very gently until the action starts, when the flame is immediately removed. Add more strong nitric acid from time to time as the reaction slackens. When the reaction is proceeding quietly, replace the flame and boil the solution until most of the nitric acid has been driven off. Dilute somewhat, filter, and evaporate until fumes cease to come off.

The syrupy liquid that remains is phosphoric acid, H_3PO_4. The nitric acid has oxidized the phosphorus first to the oxide P_2O_5 (being reduced itself in the process to the red gases that you saw evolved). The oxide P_2O_5 then reacts with water to give phosphoric acid H_3PO_4:

$$P_2O_5 + 3H_2O = 2H_3PO_4.$$

(*c*) Heat some sawdust on an iron tray until it just begins to char. Remove the flame, and pour on strong nitric acid. The whole mass is inflamed owing to the rapid oxidation.

(*d*) Add some strong nitric acid to potassium iodide solution, and note the liberation of iodine.

3. Test the action of the acid on metals.

If you remember the results of Experiment 15 you will expect the production of brown fumes instead of hydrogen as is the case with other acids.

Try to obtain hydrogen by using dilute nitric acid and magnesium in the cold.

4. Observe the action of the acid on ferrous sulphate solution. A dark brown colour is produced.

¶ Commercial Preparation of Nitric Acid.

Nitric acid is prepared commercially by the same method as is used for its laboratory preparation. Two other more modern methods of preparation are referred to under the 'Fixation of Atmospheric Nitrogen' (p. 172).

ℭ Properties.

1. Nitric acid is a colourless fairly volatile liquid. Its vapour is decomposed by light with formation of nitrogen dioxide. This decomposition is the cause of the yellow colour of the acid when it has been exposed to light for some time. The acid in a full bottle does not become yellow.

2. The acid is a strong (highly-ionized) acid, and forms a series of salts called the nitrates.

3. The acid is a powerful oxidizing agent and liberates iodine from potassium iodide. The acid converts non-metals, such as carbon, sulphur, and phosphorus, into their acid anhydrides, and metals into nitrates (or in some cases, oxides).

4. The acid reacts with a variety of complex compounds of carbon, such as sawdust, glycerin, cotton, benzene, &c. The products of these reactions are the important substances, oxalic acid, nitro-glycerin, gun-cotton, and nitro-benzene, &c.

5. The gaseous products of the reactions of nitric acid with the metals are very varied, and depend on the temperature, the metal used, the concentration of the acid, and other conditions. Hydrogen is not produced except in the case of magnesium, because when it is 'atomic', i. e. before the pairs of atoms have joined up to form molecules, it reacts with the acid and reduces it, being itself oxidized to water.

6. The acid is reduced by ferrous sulphate to nitric oxide, NO, and this substance reacts with the excess of ferrous sulphate to form an unstable dark-brown compound supposed to have the formula $FeSO_4 . NO$.

ℭ The Nitrates.

These salts are all soluble in water.

They are usually prepared by the action of nitric acid on the metal. All metals, with the exception of gold, platinum, and one or two rare metals, are dissolved by the acid.

The nitrates may equally well be prepared by the action of the acid on the oxide, hydroxide, or carbonate of the metal.

In order to find out whether a given salt is a nitrate, use is made of the fact that nitric acid is reduced by ferrous sulphate giving the gas nitric oxide, NO (see p. 166) which forms the brown compound $FeSO_4 . NO$ mentioned on p. 163.

In order to carry out the test, dissolve the salt in water, in a test-tube and add some ferrous sulphate solution. Now run in carefully some strong sulphuric acid in such a way that it does not mix with the solution but runs down the side of the tube and forms a layer at the bottom. Where the sulphuric acid is in contact with the solution nitric acid will be liberated from the dissolved salt, if it is a nitrate; the reaction described above will take place and a brown ring will be formed. This test is known as the *brown-ring test* for nitrates and nitric acid.

The behaviour of the nitrates on heating is important:

(1) The nitrates of sodium and potassium when strongly heated give up oxygen and are converted into nitrites, e. g.

$$2NaNO_3 = 2NaNO_2 + O_2.$$

(2) The nitrates of most metals (e. g. lead, copper, iron) give up oxygen and nitrogen peroxide and are converted into oxides, e. g.

$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2.$$

(3) The nitrates of the noble metals (silver, gold, platinum) when heated strongly leave the metal.

(4) Ammonium nitrate when heated breaks up into water and a gas called nitrous oxide. This behaviour will be further referred to in Chapter XXX.

$$NH_4NO_3 = N_2O + 2H_2O.$$

This substance N_2O is the first member of a series of five oxides of nitrogen.

EXPERIMENT 84.

Preparation of Nitrous Oxide, N_2O.

Heat 30–40 gm. of ammonium nitrate, with a few grams of sand, in a round-bottomed flask, and collect the gas given off over hot water.

Perform the following tests with jars of the gas:

(1) Introduce a lighted taper.

(2) Introduce a glowing splinter.

(3) See if feebly and brightly burning sulphur will continue to burn in the gas.

(4) See if phosphorus will burn in the gas.

EXPERIMENT 85.

Preparation of Nitric Oxide, NO.

Cover some copper turnings in a flask fitted with a thistle funnel and delivery tube with nitric acid diluted with its own volume of water. Collect the gas over water. Note that the brown colour produced at first in the flask disappears once all the air has been displaced. The equation for the reaction is:

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO.$$

Perform the following tests with jars of the gas:

(1) Expose a jar to the air.

(2) Introduce a lighted taper.

(3) See if feebly and brightly burning phosphorus will continue to burn in the gas.

(4) Pour one c.c. of carbon disulphide (care) into a jar and ignite.

(5) Pour ferrous sulphate solution into a jar.

EXPERIMENT 86.

Demonstration.

Preparation of Nitrogen Trioxide, N_2O_3.

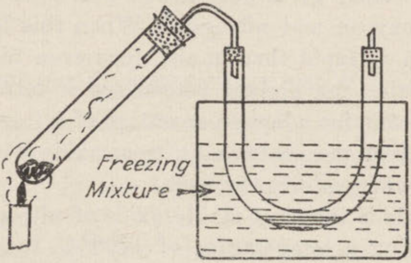
When arsenious oxide is distilled with diluted nitric acid, red vapours which condense in a freezing-mixture to a dark-blue volatile liquid, N_2O_3, are produced.

$$2HNO_3 + As_2O_3 = 2HAsO_3 + N_2O_3.$$

EXPERIMENT 87.

Preparation of Nitrogen Dioxide, NO_2.

Heat some powdered and dried lead nitrate in a hard glass tube, and pass the red gas evolved through a U-tube cooled in a freezing-mixture. A yellow liquid collects in the U-tube, and oxygen passes on and will ignite a glowing splinter held at the top of the tube.



$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2.$$

Pour the liquid oxide into a gas-jar, and note the colour changes which it undergoes on vaporizing. See if the gas will support the combustion of a taper.

EXPERIMENT 88.

Demonstration.

Preparation of Nitrogen Pentoxide, N_2O_5.

If concentrated nitric acid is distilled at a low temperature with phosphorus pentoxide, part of the distillate solidifies into white crystals of N_2O_5 on cooling in a freezing-mixture.

$$2HNO_3 + P_2O_5 = 2HPO_3 + N_2O_5.$$

ℂ The Oxides of Nitrogen as Supporters of Combustion.

The oxides of nitrogen support combustion only when the burning substance gives out enough heat to decompose the oxide into oxygen and nitrogen. When this occurs, combustion is more rapid than in air, since even nitrous oxide (which contains the highest percentage of nitrogen of the five oxides) contains a lower percentage of nitrogen than air. (Air, roughly 80 per cent., and nitrous oxide 66·67 per cent. of nitrogen when split up by heat.)

Nitric oxide is the most stable oxide of nitrogen towards heat, requiring a temperature of 1000° C. to split it up. Hence the heat given out by a lighted taper or by feebly burning phosphorus is insufficient to bring about decomposition, and these substances will not burn in the gas. Strongly burning phosphorus is, however, hot enough, and burns brilliantly in the gas. Nitrous oxide is easily decomposed by heat, decomposition starting at 520° C., and hence it will even rekindle a glowing splinter. Nitrogen dioxide extinguishes a taper, but supports the combustion of phosphorus. It is decomposed at 600°.

Nitrogen trioxide and nitrogen pentoxide decompose rapidly at ordinary temperatures as follows:

$$N_2O_3 = NO_2 + NO,$$
$$2N_2O_5 = 4NO_2 + O_2,$$

i. e. these substances do not exist as gases at ordinary temperatures, and cannot therefore be classed as supporters or non-supporters of combustion.

None of the oxides burns.

Since nitrous oxide resembles oxygen in its power of rekindling a glowing splinter we need a means of distinguishing between the gases.

If a jar of nitric oxide and a jar of oxygen are placed mouth to mouth dense brown fumes of nitrogen dioxide are immediately formed:

$$2NO + O_2 = 2NO_2.$$

There is no action if a jar of nitric oxide is placed mouth to mouth with a jar of nitrous oxide.

Hence nitric oxide can be used to distinguish between the two gases.

ℂ Volume Compositions and Formulae.

The volume composition and formula of nitrous or nitric oxide can be found by burning potassium in the gas over mercury. By this means all the oxygen is absorbed and nitrogen is left. It is found that one volume of nitrous oxide yields one volume of nitrogen, and that one volume of nitric oxide yields half a volume of nitrogen. Hence if the vapour densities of these gases are known (22 and 15) their formulae can be calculated. The student should write out the proofs as an exercise.

The properties of the oxides of nitrogen may be conveniently tabulated as shown on the following pages.

There are acids corresponding to three of the oxides of nitrogen: Thus $N_2O_5 + H_2O = 2HNO_3$: i. e. nitrogen pentoxide is the acid anhydride of nitric acid. Its reaction with water is violent. $N_2O_3 + H_2O = 2HNO_2$: i. e. nitrogen trioxide is the acid anhydride of nitrous acid. (This is the acid whose salts are the nitrites.) There is also an acid HNO called hyponitrous acid, which we should expect to be formed from nitrous oxide thus: $N_2O + H_2O = 2HNO$; but, as you will notice from the table, nitrous oxide is neutral, and does not react with water. It is not, therefore, an acid anhydride. When nitrogen dioxide reacts with water it behaves as if it were $N_2O_3 + N_2O_5$, i. e. a mixed anhydride, and gives rise to nitrous and nitric acids.

$$4NO_2 \longrightarrow N_2O_3 + N_2O_5.$$

$$N_2O_3 + N_2O_5 + 2H_2O = 2HNO_2 + 2HNO_3.$$

NITRIC ACID AND THE OXIDES OF NITROGEN

Name and Formula .	*Nitrous Oxide,* N_2O.	*Nitric Oxide,* NO.
Preparation	Heat ammonium nitrate.	Action of dilute nitric acid on copper.
Equation	$NH_4NO_3 = N_2O + 2H_2O$.	$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO$.
Colour	Colourless gas.	Colourless gas.
Smell	Sweet, faint.	Unknown.
Solubility	Somewhat soluble in cold water, collect over hot.	Insoluble.
Density	Heavier than air.	Heavier than air.
Ease of liquefaction .	Hard to liquefy.	Hard to liquefy.
Supporter of combustion	Good supporter.	Bad supporter.
Reaction with water .	None.	None.
Kind of oxide . . .	Neutral.	Neutral.
Any important properties	Used as an anaesthetic; called laughing gas or simply 'gas'.	Forms brown fumes of NO_2 immediately on exposure to air. $2NO + O_2 = 2NO_2$. Forms a brown solution containing FeSO . NO with ferrous sulphate. The pure gas can be obtained by warming this solution. When mixed with carbon disulphide and ignited gives a brightly luminous flash.

NITRIC ACID AND THE OXIDES OF NITROGEN

Nitrogen Trioxide, N_2O_3.	*Nitrogen Dioxide*, NO_2.	*Nitrogen Pentoxide*, N_2O_5.
Action of dilute nitric acid on arsenious oxide.	Heat lead nitrate.	Action of strong nitric acid on phosphorus pentoxide.
$As_2O_3 + 2HNO_3 = 2HAsO_3 + N_3O_3$.	$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$.	$2HNO_3 + P_2O_5 = 2HPO_3 + N_2O_5$.
Blue liquid at low temps., decomposed at ordinary temps.	Pale yellow liquid, changing to red-brown gas. (See below.)	White crystals at low temps., decomposed at ordinary temps.
—	Pungent.	—
Combines with water.	Reacts with water.	Combines with water.
—	Heavier than air.	—
—	Easily liquefied.	—.
—	Bad supporter.	—
$N_2O_3 + H_2O = 2HNO_2$.	$2NO_2 + H_2O = HNO_2 + HNO_3$.	$N_2O_5 + H_2O = 2HNO_3$.
Acid anhydride.	Mixed anhydride.	Acid anhydride.
—	This gas exhibits remarkable colour changes: changing from reddish-brown at 21·6° to nearly black at 40°. Above 140° the gas gets paler, until at 620° it is nearly colourless. These changes are due to changes in the composition of the molecule. E.g. $N_2O_4 \rightarrow 2\,NO_2 \rightarrow N_2 + 2O_2$.	—

ℭ The Fixation of Atmospheric Nitrogen.

In order to solve the nitrogen problem already referred to in Chapter XXIV, various methods of bringing the nitrogen of the air into combination are now employed on a large scale. These processes are said to 'fix' atmospheric nitrogen. Of these we have already mentioned one, Haber's process for the manufacture of synthetic ammonia. The ammonia may, if desired, be oxidized by air in the presence of a catalyst to nitrogen dioxide, as shown in Experiment 81, and hence to nitric acid. Another important process consists in causing nitrogen and oxygen to combine directly at the high temperature of the electric arc. The nitric oxide produced is further oxidized by the air to nitrogen dioxide. The nitrogen dioxide produced by either of these methods reacts with water and excess of air forming nitric acid:

$$4NO_2 + O_2 + 2H_2O = 4HNO_3.$$

This dilute nitric acid is often caused to act upon limestone to form calcium nitrate, which is sold as a fertilizer under the name of 'air saltpetre'.

$$CaCO_3 + 2HNO_3 = Ca(NO_3)_2 + H_2O + CO_2.$$

The direct combination of nitrogen and oxygen to form nitric oxide, and the subsequent conversion of this gas into nitric acid, also takes place when a lightning discharge passes through the air, and accounts for the 'smell of brimstone' which accompanies severe storms. Hence rain-water may contain traces of nitric acid, and this is one of the ways in which the nitrogen of the soil is renewed.

EXAMPLES ON CHAPTER XXV.

1 From the equation

$$H_2SO_4 + NaNO_3 = NaHSO_4 + HNO_3$$

calculate the weight of sodium nitrate required to yield 100 gm. of nitric acid.

2 Find the volume of hydrogen required for the complete conversion (on explosion in a eudiometer tube) of 50 c.c. of nitrous oxide to nitrogen.

3 What weight of ammonium nitrate will be required to yield 2 litres of nitrous oxide at N.T.P.?

4 What is the percentage loss of weight of potassium nitrate on heating?

5 27·5 c.c. of a solution of nitric acid were equivalent to 25 c.c. of *N*/10 caustic soda solution. What is the strength of the acid in grams per litre?

XXVI

CARBON, COAL-GAS, CARBON MONOXIDE, HYDROCARBONS

We have already mentioned that carbon has allotropic forms. There are three distinct varieties called diamond, graphite, and amorphous carbon. Diamond is found in South Africa, Brazil, and New South Wales among other places. It has been made artificially, but the process is costly, and the diamonds produced are very small and of a bad colour, so that the process does not pay. The natural crystalline shape of diamonds used in jewellery is altered by cutting, so as to produce the greatest possible amount of internal reflection of light which makes the diamond 'flash'. Real diamonds are transparent to X-rays, while sham ones are opaque. Small, bad-coloured diamonds are used for rock-drills, for cutting glass, and, when powdered, for polishing other gems.

Graphite is found in Cumberland, in California, and in many other parts of the world. It is now produced artificially on a large scale at Niagara Falls; sand and powdered coke are very strongly heated in electric furnaces. The silicon of the sand (see Chapter XXIX) first combines with the carbon to form silicon carbide. As the temperature rises this compound is decomposed, and the carbon deposited in the form of graphite. The water-power provides cheap electricity, and hence the process is a commercial success. Graphite is a dark-grey lustrous crystalline substance with a soapy feeling. It marks paper, and is therefore used for making pencils. (So-called 'lead' pencils all contain graphite, which is sometimes called black-lead or plumbago, although it contains no lead.) It is a good lubricant, especially for high temperatures at which oil would burn. Thus a sticking drawer may be made to slide in and out easily if the surfaces in contact are rubbed with a cake of 'black-lead', or even with a lead-pencil. It is used for polishing iron-work (polishing grates, &c.). Being a good conductor of heat and electricity it is used for making electrodes and for the cores of carbons for electric arcs.

There are many varieties of amorphous carbon containing a more or less high percentage of pure carbon. We may group them as follows:

- A. The Charcoals.
    - Wood Charcoal.
    - Coco-nut Charcoal.
    - Vine Charcoal.
    - Sugar Charcoal.
    - Animal Charcoal.
- B. Coal and its derivatives.
    - Coal.
    - Coke.
    - Gas-carbon.
    - Jet.
- C. Lamp-black, acetylene-black, and soot.

Wood Charcoal is used: (1) as a fuel, in countries where wood is abundant. Formerly it was made in a primitive way by causing stacks of wood covered with turf to burn very slowly. In this process all the valuable volatile products produced at the same time are lost, and in modern processes the wood is heated in iron retorts out of contact with air, and the volatile products, consisting mainly of wood spirit, acetic acid, and acetone (used as a solvent) are carefully collected. It is also used (2) for the reduction of metals from their oxides, both on a large scale, and in the laboratory when oxides are reduced by heating on charcoal.

Thus if lead oxide is heated on charcoal, the following reaction takes place: $2PbO + C = CO_2 + 2Pb$. The lead appears in tiny metallic beads which mark paper. (3) For preserving wood: thus wooden piles for piers, &c., may be charred, and will then successfully resist the action of air and sea-water. (4) For absorbing gases: owing to its porous nature charcoal, and especially *coco-nut charcoal*, can absorb many times its own volume of gas. It is therefore used in filters, in gas-masks, and, when growing bulbs in bowls, to remove noxious gases.

Vine Charcoal made from the shoots of vines is used by artists in sketching out oil-paintings on canvas.

Sugar Charcoal when carefully prepared by charring cane sugar is very pure carbon, and is used as such in the laboratory.

Animal Charcoal, or bone-black, is the residue left when bones are distilled. It contains only about 10 per cent. of carbon, but a high percentage (80 per cent.) of calcium phosphate. It has the property of absorbing vegetable colouring matters from solution, and is used to make white sugar from brown.

Different varieties of *coal* contain different percentages of carbon, anthracite containing as much as 90 per cent. and more. Coal has been made by the decay of vegetable matter in remote ages. The first stages in the decomposition are probably brought about by bacteria, and the later ones by heat and high pressure. When coal is distilled (i. e. heated in a retort out of contact with air) for the manufacture of coal-gas, *coke* and *gas-carbon* used for electrodes, are two important by-products. *Jet* is a hard naturally-occurring form of coal used for making ornaments.

Lamp-black is produced by burning oils rich in carbon in a limited supply of air. It is used for making black paint and printers' ink.

Acetylene-black, formed when acetylene is exploded by pressure, is used for the same purposes. Ordinary *soot* is used to protect seedlings from slugs and as a fertilizer, since it is rich in ammonium compounds.

The three allotropic forms of carbon can be shown to be chemically the same because the same weight of each, when pure, if burnt in oxygen yields the same weight of carbon dioxide and nothing else. The production of carbon dioxide on heating in air or oxygen is the test if we wish to find out whether a compound contains carbon.

The substance to be tested, if a solid, may be

either (1) Heated in a deflagrating spoon, and, when burning, lowered into a gas-jar containing lime-water;

or (2) Heated in a hard glass tube, and the gas evolved led into lime-water;

or (3) If it will not give off carbon dioxide when heated alone, mixed with copper oxide, which will help to oxidize the carbon if present to carbon dioxide, and heated as in (2).

(4) Failing any of these methods, mixed with copper oxide, and heated in a stream of oxygen.

A liquid may be burnt in a capsule over lime-water, or made into a paste with copper oxide, and treated as above.

A gas can be burnt at a jet in a gas-jar over lime-water.

EXPERIMENT 89.

Heat some coal strongly in a test-tube. Notice that the issuing gas is inflammable. Note the formation of coal-tar.

❡ The Manufacture of Coal-gas.

Coal is heated out of contact with air in a fire-clay retort. Near the front of the retort a vertical pipe, called a stand-pipe, leads out the volatile products. A number of retorts are built into a stack, and the stand-pipes from every retort in a stack lead down through dip-pipes into the hydraulic main, a transverse section of which is seen in Fig. 1. This main is a long covered trough containing water which acts as a seal for the ends of the dip-pipes. Coal-tar collects below the water, and ammonia compounds dissolve in it. A longitudinal section of the hydraulic main is shown in Fig. 2.

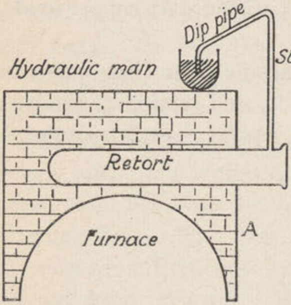


Fig. 1.

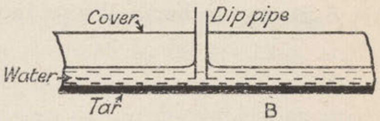


Fig. 2.

After passing through the hydraulic main the gas is thoroughly cooled so that all tar may be deposited, and is then purified from sulphuretted hydrogen, carbon dioxide, and other impurities. The gas is stored in the so-called 'gasometers' over water. The residue left in the retort consists of coke, and possibly some hard gas-carbon may form in the cooler parts of the retort. The coal-tar is an extremely valuable by-product, from which are manufactured such diverse products as dyes, drugs (e. g. aspirin, saccharin), essences (cinnamon), anaesthetics (novocaine), explosives (lyddite), &c. The ammoniacal liquor, as already stated (Chapter XXIII) supplies the ammonia of commerce. It is boiled with lime, and the ammonia gas liberated is sent into dilute sulphuric acid to form ammonium sulphate.

Coal-gas is a mixture of gases, mostly hydrocarbons, with hydrogen. The products of its combustion are carbon dioxide and moisture, as may readily be shown (1) by lowering a burning jet of the gas into a jar of lime-water, removing the jet and shaking up, when the lime-water will be found to have gone milky, owing to the formation of calcium carbonate; and (2) by lowering a burning jet of the gas into a dry jar when the moisture formed will be seen on the sides.

ℂ Carbon Monoxide.

Every one who read the papers during the latter part of 1922 and first part of 1923 will have noticed constant reference to the presence of carbon monoxide in coal-gas. This oxide of carbon can readily be prepared in the laboratory.

EXPERIMENT 90.

Preparation of Carbon Monoxide.

Caution: This gas is extremely poisonous.

Place a *small* quantity of oxalic acid in a test-tube, cover with strong sulphuric acid, fit with a cork and bent tube, and heat gently. Ignite the issuing gas, and note that it burns with a blue flame. Blow out the flame, and pass the gas into lime-water. Note that it becomes cloudy, showing that carbon dioxide is produced at the same time. This is an example of the dehydrating action of strong sulphuric acid:

$$C_2O_4H_2 \,.\, 2H_2O \rightarrow CO + CO_2 + 3H_2O,$$

the three molecules of water being taken up by the acid. If it is desired to prepare jars of the gas, this must be done in a fume cupboard, and only if special permission is given. The gas should be passed through caustic soda to absorb and remove carbon dioxide.

The action of strong sulphuric acid on formic acid is similar, and results in the production of pure carbon monoxide:

$$H_2CO_2 \rightarrow H_2O + CO.$$

There are other methods of preparation of this gas, notably by sending steam over red-hot coke:

$$C + H_2O = CO + H_2.$$

The mixture of carbon monoxide and hydrogen is called water-gas, and this gas is often mixed with the coal-gas supplied for illuminating purposes. Water-gas gives out a great deal of heat when it is burnt, the reactions taking place in accordance with the equations:

$$2CO + O_2 = 2CO_2.$$
$$2H_2 + O_2 = 2H_2O.$$

It does not add materially to the luminosity of the coal-gas. If air is sent over red-hot coke a mixture of carbon monoxide and nitrogen, called producer gas, is obtained. This reaction may be seen in an ordinary coal fire. In the lower part of the fire the carbon burns with excess of oxygen to carbon dioxide, but as this gas passes up through the layers of heated coal it is reduced to carbon monoxide:

$$CO_2 + C = 2CO.$$

This carbon monoxide then burns with the familiar blue flame of the coal fire, and carbon dioxide is formed once more and passes up the chimney: $2CO + O_2 = 2CO_2$.

The danger of ill-ventilated stoves is from the escape of carbon monoxide into the air of a room owing to there being an insufficient supply of air to burn it to carbon dioxide. Producer gas is used for heating in factories and for driving gas-engines.

❡ Comparison of the Oxides of Carbon.

Carbon Monoxide.	*Carbon Dioxide.*
Physical.	
Colourless.	Colourless.
No smell.	Faint pungent smell.
Insoluble.	Fairly soluble.
Lighter than air.	Heavier than air.
Hard to liquefy.	Easy to liquefy.
Chemical.	
Neutral oxide.	Acid oxide.
Burns with blue flame to carbon dioxide.	Does not burn.
Does not support combustion.	Does not support combustion.
No effect on lime-water.	Turns lime-water milky.
Not absorbed by caustic soda and caustic potash.	Absorbed by caustic soda and caustic potash.
Poisonous.	Not poisonous.

❡ Hydrocarbons.

The two facts we have mentioned so far with regard to hydrocarbons are :

(1) That they burn in air forming carbon dioxide and water ;

(2) That they burn in chlorine forming hydrochloric acid and setting free carbon (cf. page 92.)

There is a large number of these substances, and they occur naturally in vast quantities as petroleum and as natural gas. Petroleum is a mixture of hydrocarbons from which petrol and many other useful products are obtained by distilling and collecting the portions coming over at definite temperatures. There are also solid hydrocarbons, such as paraffin wax.

EXAMPLES ON CHAPTER XXVI.

1 What volume of oxygen is required for the complete combustion of a litre of carbon monoxide?

2 The equation representing the combustion of a hydrocarbon, butane, C_4H_{10}, is

$$2\,C_4H_{10} + 13\,O_2 = 8\,CO_2 + 10\,H_2O.$$

If 200 c.c. of the hydrocarbon are exploded with 1300 c.c. of oxygen and the explosion tube cooled, what will be

(*a*) the volume after explosion;

(*b*) the volume after shaking up with caustic potash solution?

XXVII

FLAME: THE BLOWPIPE

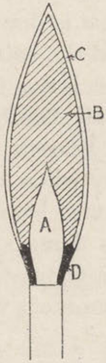
It is a matter of common experience that different materials require to be heated to different temperatures before they will ignite. Thus phosphorus ignites at 34°, and charcoal not till 360°. This temperature is spoken of as the ignition temperature of the substance.

Flame is gas raised by the process of its own combustion to the temperature of incandescence. Before the combustion commences heat must be applied in sufficient quantity to raise the gas to its ignition point. An examination of the flame of a Bunsen burner (luminous) and of a candle will throw light on the structure of these flames.

EXPERIMENT 91.

Close the holes at the base of a Bunsen burner, and light the issuing gas. Shield from draughts, and note the following regions in the flame:

A. A non-luminous zone of unburnt gas which is quite cool. The unburnt gas can be led off through a glass tube and ignited. A platinum wire will not get red-hot in this region.



B. A luminous zone containing unburnt carbon which will be deposited on a piece of porcelain held in it. This zone is very hot (platinum wire). In this zone the hydrocarbons and hydrogen are burning, but as the supply of air is limited, combustion is incomplete, and we get 'charring', i. e. carbon is present in this zone.

C. An outer, hot, non-luminous zone in which unburnt gases and carbon from B are completely burnt.

D. A deep blue region in which combustion occurs.

These four regions can also be distinguished in a candle flame in which 'candle gas' (vaporized wax) is burnt. The wick of a burning candle bends over sideways because it is plaited more tightly on one side than the other. Thus the tip of the wick gets to the edge of the flame, and is burnt away, avoiding the necessity of snuffing the candle.

Students will now realize the folly of pressing the Bunsen flame close up under a vessel to be heated, since this brings a cold region in contact with the vessel.

In the non-luminous Bunsen flame there are only two zones, the inner one a zone of no combustion, and the outer one a zone of complete combustion. This flame is hotter than the luminous flame because the gases in it get the air necessary for combustion both from the surrounding atmosphere and from the air that is drawn up into the interior of the flame from the holes at the bottom of the burner.

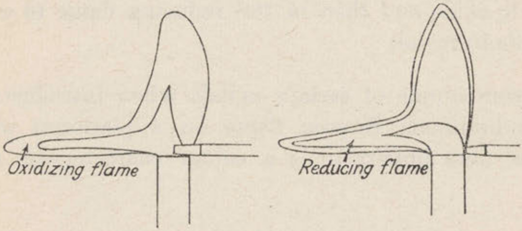
The luminosity of flames is due in part to the presence of solid particles. We are all familiar with the luminosity imparted to an ordinary Bunsen flame by a 'mantle' of solids which glow brightly when heated. Cooling a flame lessens its luminosity, as may be shown by pressing a cold surface on to a luminous flame. Increase of pressure increases the luminosity of a flame, the flames of both alcohol and hydrogen becoming luminous under pressure.

EXPERIMENT 92.

Light a candle, and depress a small coil of copper wire over the wick. Note that the candle goes out owing to the cooling effect of copper, which is a good conductor.

Light a Bunsen burner, and press down on the flame a piece of wire-gauze. Note that when the gauze gets white-hot the flame passes through. Hold a piece of gauze a little way above the top of a burner, and light the gas above the gauze. Note that there is no flame below the gauze.

A flame will not pass through wire-gauze until it is nearly white-hot, owing to the fact that the rapid conducting away of the heat lowers the temperature of the gas below its ignition point. This principle is made use of in the Davy Lamp, which consists of an oil lamp inside a cylinder of wire-gauze. The air in mines often contains inflammable hydrocarbons, and is then called 'fire-damp'. An ordinary lamp would ignite the fire-damp, but with the Davy Lamp inflammable gases may get inside the wire gauze and ignite but the flame so produced is cooled below the ignition point when it attempts to burn back through the gauze.



The blowpipe flame is obtained by directing a jet of air into the luminous flame. It may be either an oxidizing or a reducing flame.

To obtain an oxidizing flame, place the nozzle of the blowpipe at the centre of the flame, resting on the burner, and blow hard. A small non-luminous flame is formed whose outer mantle is the oxidizing flame.

To obtain a reducing flame, place the nozzle just outside the top of the burner, and blow gently. A small luminous flame is obtained whose yellow region contains hot particles of unburnt carbon which perform the reduction.

Experiment 93.

Place a small pinch of lead oxide in a cavity on a block of charcoal. Make it red-hot with the oxidizing flame, and then heat it for some time in the reducing flame. A globule of metallic lead will be obtained, often called a 'lead bead'. It will mark paper. The lead oxide has been reduced to lead: $2PbO + C = CO_2 + 2Pb$. If we wish to reduce a salt instead of an oxide, we mix with dry sodium carbonate or fusion mixture (sodium and potassium carbonates), and heat first in the oxidizing flame, to convert the salt into the carbonate by double decomposition and to convert the carbonate to oxide and then in the reducing flame to convert the oxide to metal.

The compounds of certain metals when introduced into the non-luminous Bunsen flame on a platinum wire or asbestos fibre impart to it a colour characteristic of the metal.

Experiment 94.

Moisten a small quantity of a compound of each of the following metals with dilute hydrochloric acid, and bring into the outer edge of the non-luminous Bunsen flame on a clean asbestos fibre or platinum wire.

Barium	(apple-green).
Copper	(blue-green).
Strontium	(crimson).
Calcium	(brick-red).
Potassium	(lilac).
Lead	(blue).
Sodium	(golden-yellow).

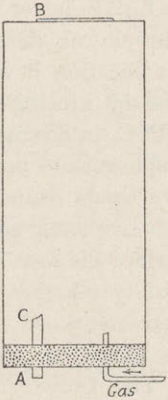
The colours characteristic of these metals should be learnt off by heart.

The terms 'supporter of combustion' and 'combustible' are interchangeable, thus air can be made to burn in coal-gas.

EXPERIMENT 95.

Demonstration.

If gas is sent into the lamp glass as shown with the lid on top closed, the issuing gas can be lit at A. If the lid is opened, and the light applied at B, the flame runs back up the tube AC and air burns at C in an atmosphere of coal-gas.



In this case we should call the coal-gas the supporter of combustion, and the air combustible; in the ordinary way the terms are reversed.

XXVIII

PHOSPHORUS. CHEMICAL FAMILIES

The element phosphorus has two well-marked allotropic forms called red and white phosphorus respectively. White phosphorus is manufactured from naturally-occurring phosphates by strong heating with sand and coke in an electric furnace. The carbon reduces the phosphate to phosphorus, and the sand acts as a flux to lower the melting-point of the mass. The crude phosphorus distils off and is collected under water; after purification it is cast into sticks. Red phosphorus is obtained by heating white phosphorus with great care to about 250° C. in absence of air.

Both kinds of phosphorus are used for making matches; ordinary matches have heads containing white phosphorus made into a paste with oxidizing agents. When these are rubbed on a rough surface the heat produced is sufficient to ignite the match. Safety matches contain no phosphorus on the heads, which are composed of a mixture of oxidizing and reducing agents, such as potassium chlorate and antimony sulphide. The brown material on which the matches 'strike' is composed of red phosphorus, powdered glass and glue. When the match head is rubbed on this surface, sufficient heat is generated to cause oxidation of the red phosphorus by potassium chlorate in the match head. The heat of this reaction is sufficient to start the reaction between the chlorate and the antimony sulphide. The heat of this reaction ignites the match.

In many countries the use of white phosphorus for making matches is forbidden, since the workmen are often affected by a disease of the jaw caused by the poisonous fumes of this kind of phosphorus.

❡ Comparison of Red and White Phosphorus.

Red.	*White.*
Dark red powder.	Wax-like white or yellow solid.
S.G. 2·25.	S.G. 1·82.
Ignition temp., 240° C.	Ignition temp., 34° C.
Melting-point, 589·5° C. under 43 atmospheres pressure.	Melting-point under water, 43° C.
Insoluble in water.	Insoluble in water.
Insoluble in carbon disulphide.	Soluble in carbon disulphide and in oil.
Not poisonous.	Poisonous.
No action with boiling alkali.	Reacts with boiling alkali, $3NaOH + 4P + 3H_2O = \underset{\text{Sod. hypophosphite.}}{3NaH_2PO_2} + PH_3$
Slowly oxidized by air, without phosphorescence, becoming moist and forming phosphoric acid.	Rapidly oxidized by air with phosphorescence, therefore always kept under water.

Of the numerous compounds of phosphorus we shall only consider three, namely phosphorus pentoxide, phosphine, and phosphoric acid.

❡ Phosphorus Pentoxide, P_2O_5.

Phosphorus pentoxide is prepared by the combustion of phosphorus in air. In the laboratory a suitable method is to ignite some phosphorus resting on a piece of porcelain on a sheet of clean glass and to cover it with a dry bell-jar. The oxide settles as a white powder. Its most characteristic property is its great affinity for water. When exposed to moist air it becomes covered with white viscous metaphosphoric acid, HPO_3. When thrown into cold water there is a violent action, metaphosphoric acid being first formed, and on boiling or long standing, orthophosphoric acid:

$$P_2O_5 + 3H_2O = 2H_3PO_4 \text{ (on boiling).}$$

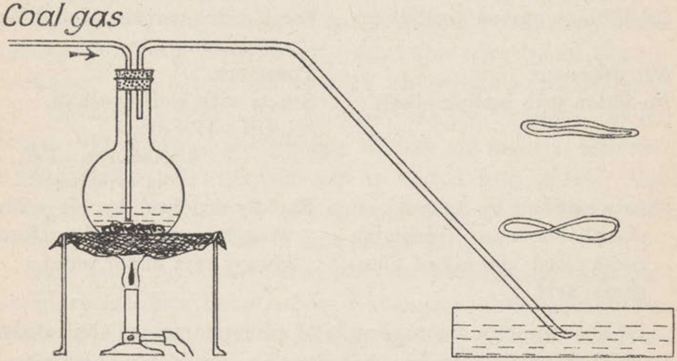
◖ Phosphine, PH_3.

EXPERIMENT 96.

Demonstration.

Preparation of Phosphine.

Pieces of white phosphorus are placed in a flask and covered with 40 per cent. caustic soda solution. The air is swept out by coal-gas, and the flask is then heated. After a little time the bubbles of gas issuing from the end of the delivery tube ignite spontaneously and form smoke rings. In order to get these rings a good shape a long delivery tube is used, so that the air currents near the flame shall not disturb them. The bore of the tube also should be large, so that large rings may be obtained. The end of the tube must dip just under water, so as to avoid the danger of the flame striking back and causing an explosion. At the end of the experiment the phosphine must all be swept out of the flask by coal-gas before air is admitted.



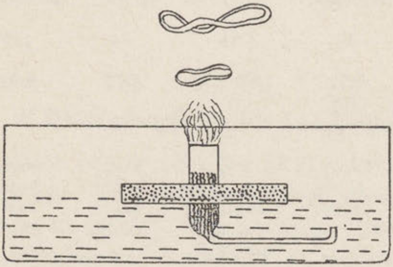
The spontaneously inflammable gas, phosphine, produced in the above reaction has a composition expressed by the formula PH_3. Note the similarity of this formula to that of ammonia NH_3. When phosphine burns, phosphorus pentoxide (which forms the 'smoke rings') and water are formed:

$$2PH_3 + 4O_2 \rightarrow P_2O_5 + 3H_2O.$$

Experiment 97.

How to make a 'Holmes Signal'.

Draw out a piece of tubing about a centimetre in diameter into the form shown. Pass it through a shallow cork bung and place inside it some powdered calcium phosphide. Float on water in the sink, and note that the phosphine produced is spontaneously inflammable. The residue is mostly calcium hydroxide.



ℭ Chemical Families. Nitrogen and Phosphorus.

The student will have noticed that phosphorus and nitrogen pentoxides, and phosphine and ammonia, have similar formulae. In the pentoxides both elements are pentavalent, and in the hydrogen compounds, trivalent. A similarity in valency is the principal similarity between the two elements, both of which are members of a chemical 'family'. The other members are arsenic, antimony, and bismuth. There is a gradual change in properties as we pass from one member of the family to the next, as shown in the following table:

	Nitrogen.	*Phosphorus.*	*Arsenic.*	*Antimony.*	*Bismuth.*
Atomic weight	14	31	74	119	206
Density	0.79 (liq. nitrogen)	1·82–2·25	5·73	6·62	9·80
Formula and character of pentoxide	N_2O_5 acid oxide.	P_2O_5 acid oxide less strongly acid than N_2O_5.	As_2O_5 feebly acid oxide.	Sb_2O_5 feebly basic oxide.	Bi_2O_5 basic oxide.
Formula and character of hydride	NH_3 strongly basic.	PH_3 feebly basic.	AsH_3 not basic.	SbH_3 not basic.	BiH_3

We might trace the gradual progress in properties in other chemical and physical characteristics, but enough has been given to justify the term 'family' for these five elements. We shall now make in greater detail a comparison between ammonia and phosphine.

Ammonia.	*Phosphine.*
Physical Properties.	
Colourless gas.	Colourless gas.
Pungent smell.	Smell of bad fish.
Very soluble.	Insoluble.
Lighter than air.	Heavier than air.
Easily liquefied.	Hard to liquefy.

Ammonia.	*Phosphine.*
Chemical Properties.	
Does not burn in air.	Ignites at 100° C., but the gas produced by ordinary laboratory methods is impure, and ignites spontaneously.
Does not support combustion.	Does not support combustion.
Solution in water is strongly basic, and contains NH_4OH.	Forms no compound corresponding to NH_4OH.
Solution in water reacts with acids to form stable ammonium salts.	Reacts with gaseous hydrochloric (but not sulphuric or nitric) acid to form unstable phosphonium salts.

Phosphoric Acid. H_3PO_4.

The preparation of this acid has already been undertaken in Experiment 83. The acid when pure consists of white crystals melting at 38·6° C., which readily dissolve in water, but as ordinarily prepared it consists of a syrupy liquid, from which crystals are only obtained with difficulty. The acid is a weak, tribasic acid, forming three sets of salts. The sodium phosphates are:

normal sodium phosphate Na_3PO_4.
disodium hydrogen phosphate Na_2PO_4.
sodium dihydrogen phosphate NaH_2PO_4.

Chemical Families: The Halogens.

Before closing the chapter we must give an example of a Chemical Family in which all the members are non-metals. They are called the 'Halogens' or salt-forming elements, and we have already studied one characteristic member, chlorine. The other members are fluorine, bromine, and iodine. Chlorine occupies the place between fluorine and bromine, as shown in the following table:

	Fluorine.	*Chlorine.*	*Bromine.*	*Iodine.*
Atomic weight	19	35·5	80	127
Valency . . .	Monovalent.	Monovalent.	Monovalent.	Monovalent.
Colour and physical state	Colourless gas.	Greenish yellow gas.	Red-brown liquid.	Greyish-black solid.
Action with hydrogen	Explodes.	Explodes when lit or in bright sunlight.	Combines when strongly heated.	Combines when heated in presence of a catalyst.
Forms a monobasic acid	HF hydrofluoric.	HCl hydrochloric.	HBr hydrobromic.	HI hydriodic.

Of these acids hydrofluoric is the most and hydriodic the least stable, the other two being intermediate in the order given.

EXAMPLE ON CHAPTER XXVIII.

Excess of phosphorus was placed in a closed vessel containing air of volume 1000 c.c., and sealed up at N.T.P. The globe was warmed to ignite the phosphorus, and when combustion was complete it was cooled to 9° C. Air contains 21 per cent. of oxygen by volume (roughly). What was the final pressure in the globe ?

XXIX

SILICA: GLASS: FINDING A FORMULA FROM A GIVEN PERCENTAGE COMPOSITION

Silicon is, next to oxygen, the most abundant element in the earth's crust. It is an element belonging to the same family as carbon, and forms a large number of compounds which resemble the corresponding carbon compounds. Of these compounds we shall only consider silica, SiO_2, the oxide of silicon which is analogous with carbon dioxide, and which occurs in nature in vast quantities as rock-crystal, quartz, sand, flint, &c. It can also be made in the laboratory as a white amorphous powder. If this is fused in the oxyhydrogen flame, a glassy mass which can be made into laboratory apparatus is obtained. The advantages of this apparatus over glass-ware are (1) that it can be heated to redness and quenched in cold water without breaking, and (2) that it is unaffected by the strongest acids, except hydrofluoric acid. It is, however, attacked by alkalies, so that it cannot even be used for heating sodium bicarbonate to convert it into normal carbonate. The alkali converts the silica into a silicate (sodium silicate is sold as 'water-glass' for preserving eggs):

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2.$$

Silica is thus an acid oxide.

Since it is almost totally non-volatile it can displace more volatile acid oxides from their salts: thus it will drive sulphur trioxide out of sulphates:

$$Na_2SO_4 + SiO_2 = Na_2SiO_3 + SO_3.$$

Silica in the form of white sand is present in all forms of glass. The sand is fused with any alkali, such as potassium or sodium carbonate, and with lime or lead oxide. On cooling, a hard, transparent, non-crystalline glass is obtained, which can be shaped at a red-heat. The different varieties of glass are produced by varying the amounts of the different ingredients, thus flint glass, used for making lenses, contains a considerable amount of lead oxide, but being readily acted on by acids and alkalies, it is not used for chemical apparatus. It is really a potash-lead silicate. Hard glass for combustion tubes is a potash-lime silicate.

There is a very large number of naturally occurring silicates, among which we may mention talc, $H_2Mg_3(SiO_3)_4$, mica, $KH_2Al_3(SiO_4)_3$, asbestos, felspar, and clay.

A glance at the formulae of talc and mica shows them to be highly complex substances. The student may inquire how these formulae are determined. Once an analysis of the mineral has been carried out, its percentage composition can be determined. Now it is clear that the numbers of atoms of any element present in a molecule are inversely proportional to the weights of the atoms. Let us take the simple case of sodium silicate, Na_2SiO_3. Analysis shows the percentage composition to be:

Sodium	37·71 per cent.
Silicon	22·95 ,,
Oxygen	39·34 ,,

Divide each weight by the atomic weight of the element. Then the ratio of the *numbers of atoms* of Sodium : Silicon : Oxygen will be

$$\frac{37{\cdot}71}{23} : \frac{22{\cdot}95}{28} : \frac{39{\cdot}34}{16} = 1{\cdot}64 : 0{\cdot}82 : 2{\cdot}46.$$

The numbers of atoms must be whole numbers, since by hypothesis an atom cannot be divided, and by inspection the ratio is clearly 2 : 1 : 3. Hence the formula is Na_2SiO_3.

EXAMPLES ON CHAPTER XXIX.

1 Find the formula of a substance whose percentage composition is:

Calcium	38·71 per cent.
Phosphorus	20·00 "
Oxygen	41·29 "

2 Find the formula of a substance whose percentage composition is:

Hydrogen	5·88 per cent.
Oxygen	94·12 "

and molecular weight 34.

3 Crystalline magnesium sulphate contains 51·22 per cent. of water. The anhydrous sulphate has the formula $MgSO_4$. How many molecules of water of crystallization are there?

4 Find the formula of a substance whose percentage composition is:

Carbon	52·18 per cent.
Hydrogen	13·04 "
Oxygen	34·78 "

and molecular weight 46.

XXX

METALS AND NON-METALS

SODIUM AND ITS PRINCIPAL COMPOUNDS

COMPARISON OF SODIUM WITH POTASSIUM AND AMMONIUM.

We have previously concerned ourselves mainly with the chemistry of the non-metals, and before starting on a study of a few of the commoner metals it will be well to sum up the most important differences between these two classes of elements.

	Non-Metals.		*Metals.*
1	Frequently gases or solids with low melting- and boiling-points.	1	Usually solids with high melting- and boiling-points.
2	Usually brittle and not lustrous.	2	Usually hard, malleable and ductile, and lustrous.
3	Frequently have allotropic forms.	3	Rarely have allotropic forms.
4	Oxides always acidic.	4	Always at least one basic oxide: may have acid oxides as well.
5	Chlorides decomposed by water.	5	Chlorides stable in water.

It should be noted that as regards physical properties there is no hard and fast line of division between metals and non-metals: the one deciding fact is whether or no the element forms a basic oxide.

EXPERIMENT 98.

Demonstration.

Cut small pieces of sodium and potassium; note their bright lustre, lay them on watch-glasses, and leave exposed to the air for some days.

EXPERIMENT 99.

Demonstration.

Throw a small piece of potassium on water. Note that it floats and gives off a gas which ignites spontaneously, the flame having the characteristic colour imparted by potassium. When the action has ceased, test the water with litmus: it will be found to be alkaline. Repeat the experiment with sodium: the gas given off will not in general ignite spontaneously, but burns with the characteristic sodium colour when lit.

The reactions taking place are:

$$2K + 2H_2O = 2KOH + H_2.$$
$$2Na + 2H_2O = 2NaOH + H_2.$$

In order to show the production of hydrogen by the action of sodium on water, the following experiment may be carried out with great precautions, as explosions are very liable to occur.

Experiment 100.

Demonstration. (Caution!)

Cut a piece of sodium no larger than a *small* pea, and press it into a short length of quarter of an inch lead tubing, closed at one end. Hold with tongs in a trough under an inverted jar of water. Hydrogen collects in the jar, and can be tested for in the usual way.

Metallic sodium and potassium are soft, greyish-white metals which melt at low temperatures. Their surfaces when freshly cut are quickly tarnished, and the metals are converted by moist air to the hydroxides. The carbon dioxide of the air is then absorbed by these hydroxides, and if the products of Experiment 98 are examined after some days, both will effervesce with acids, liberating the carbon dioxide. The potassium carbonate is deliquescent (i. e. takes up water from the air), and the residue from the potassium is therefore wet, while the sodium residue is dry. It should be noted that the salts of potassium are in general more soluble than the corresponding sodium salts, and that potassium has the greater chemical activity of the two, as seen in its action on water. Both metals are kept under mineral oil to exclude them from air and moisture. Acids act on both metals with dangerous violence. Both metals burn in air or oxygen, and also in chlorine. Both metals are uniformly monovalent, and all their common salts are soluble.

EXPERIMENT 101.

Preparation o Caustic Soda from Sodium Carbonate.

Weigh out roughly 10 gm. of sodium carbonate, dissolve in 100 c.c. of water, and boil. To the boiling solution add gradually, with stirring, about 20 gm. of slaked lime made into a very thin paste with water. Boil for a few minutes, let the mixture settle, and decant off the clear liquid. The reaction is as follows :

$$Na_2CO_3 + Ca(OH)_2 = 2NaOH + CaCO_3.$$

The insoluble calcium carbonate is precipitated.

Preserve the solution in a bottle with greased stopper for future use.

Caustic soda is a white deliquescent solid. When exposed to air for some time it first becomes surrounded by a strong solution of the hydroxide, and this then takes up carbon dioxide from the air, sparingly soluble sodium bicarbonate being formed, and after a while the piece of caustic soda appears covered with a dry white coating.

Caustic soda is a strong (highly ionized) base, exhibiting to a marked degree all the general properties of bases (Chapter XVIII). Its action on oils and fats, forming soaps, is extremely important, as it is the alkali used in soap-making (Experiment 40).

The other more important reactions of this substance are :

(1) Action with acids forming sodium salts.

$$NaOH + HCl = NaCl + H_2O.$$

(2) Action with carbon dioxide and sulphur dioxide, which it absorbs (Chapter XXII).

$$NaOH + CO_2 = NaHCO_3.$$
$$2NaOH + CO_2 = Na_2CO_3 + H_2O.$$

(3) Action with chlorine, which it absorbs.

If chlorine is sent into a hot, strong solution of caustic soda, sodium chlorate is one of the products (see Chapter XXXI). This is not a very important substance, but the corresponding potassium salt, produced in a similar manner from potassium hydroxide, is very important, and is one of the oxidizing agents used in making matches.

(4) Action on zinc and aluminium, resulting in liberation of hydrogen (Chapter XXXI).

(5) Action on solutions of metallic salts, precipitating hydroxides which are often insoluble; e. g. ferric hydroxide from ferric chloride solution.

$$FeCl_3 + 3NaOH = Fe(OH)_3 + 3NaCl.$$

[Balanced action: see Chapter XII.]

(6) Action on ammonium compounds, with liberation of ammonia.

$$NH_4Cl + NaOH = NH_3 + NaCl + H_2O.$$

There are several different methods of manufacturing sodium carbonate, but the only one we shall discuss here is the latest to be worked on the manufacturing scale. It consists in the electrolysis of a strong brine in such a way that the sodium forms sodium hydroxide, cf. Experiment 60 and the subsequent passing into this solution of carbon dioxide. Its white crystals are familiar as washing soda, $Na_2CO_3 . 10H_2O$. On exposure to air the crystals effloresce, that is to say they lose some of their water of crystallization, and fall to a powder. If required pure and anhydrous for volumetric work, sodium carbonate is best prepared by strongly heating the bicarbonate until there is no further loss of weight.

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

The student should read again what was said in Chapter X about the properties of the two carbonates of sodium. Remember that the carbonates of all metals except sodium and potassium give off carbon dioxide on heating, and leave the metallic oxide. Read also what was said about sodium chloride in Chapter XVII.

The compounds of potassium are not the only ones which closely resemble those of sodium ; those of ammonium are also very similar.

For instance, ammonium hydroxide, NH_4OH, is a basic hydroxide resembling caustic soda and caustic potash, and the ammonium salts, like those of sodium and potassium, are all soluble. Ammonium chloride may be caused to take up the same crystalline shape as sodium and potassium chlorides, and ammonium sulphate has the same crystalline shape as potassium sulphate. The ammonium salts, however, behave differently on heating. Thus potassium and sodium nitrates, when strongly heated, give up oxygen and form the nitrite,

$$2KNO_3 = 2KNO_2 + O_2,$$

but ammonium nitrate decomposes completely into nitrous oxide and water.

Its first tendency is to decompose into ammonia and nitric acid thus :

$$NH_4NO_3 = NH_3 + HNO_3.$$

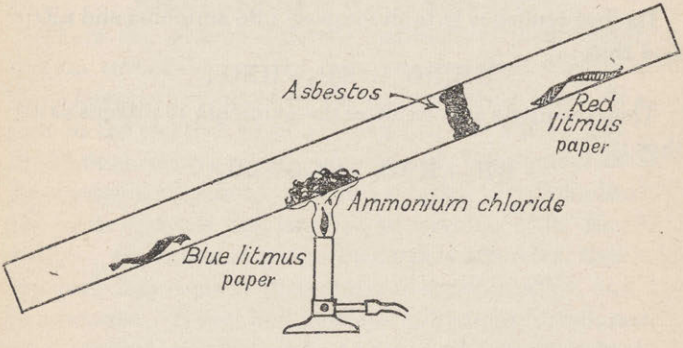
Then the nitric acid oxidizes the ammonia to nitrous oxide thus :

$$NH_3 + HNO_3 = N_2O + 2H_2O.$$

EXPERIMENT 102.

Behaviour of Ammonium Chloride on Heating.

Place a plug of asbestos in the middle of a hard glass tube, and place on one side of it some ammonium chloride and a blue litmus paper, and on the other side a red litmus paper. Heat the ammonium chloride, and note that the blue litmus paper turns red, and the red one blue.



The explanation of this fact is that ammonium chloride splits up, or dissociates on heating into ammonia and hydrochloric acid thus: $NH_4Cl \rightleftarrows NH_3 + HCl$. This is another example of a balanced or reversible reaction.

Graham's Law of Diffusion of gases states the fact that their rates of diffusion are inversely as the square roots of their densities, in other words a light gas diffuses more quickly than a heavy gas.

Now the Vapour Density of ammonia $= \frac{1}{2} \times (14 + 3)$

(since *V.D.* = half the Molecular Weight, Chapter XIX)

$$= \frac{1}{2} \times 17 = 8{\cdot}5.$$

And the Vapour Density of hydrochloric acid gas $= \frac{1}{2}(1 + 35{\cdot}5)$

$$= \frac{1}{2} \times 36{\cdot}5 = 18{\cdot}25.$$

Therefore the lighter gas, ammonia, can diffuse through the asbestos plug more quickly than the heavier hydrochloric acid. Thus the upper piece of litmus is turned blue, and the lower one red by the excess of hydrochloric acid left behind.

Decomposition into ammonia and the acid is characteristic of the behaviour of ammonium salts on heating. With ammonium carbonate the decomposition takes place rapidly at ordinary temperatures, and the solid smells strongly of ammonia.

Some ammonium compounds sublime, i. e. turn from the gaseous to the solid state without passing through an intermediate liquid state.

ℂ History and Uses of Sodium and Potassium and their Compounds.

Sir Humphry Davy, inventor of the Davy Lamp, first obtained these metals by electrolysis of the fused hydroxides early in the nineteenth century.

Sodium bicarbonate is used in medicine and in cooking, being the main constituent of baking powder. (Cf. p. 59.)

Sodium carbonate is used as a cleanser and water softener and in glass-making.

Sodium chloride is used to preserve and season food, as a source of all sodium compounds, and for the preparation of chlorine.

Sodium hydroxide is used for making soap.

Sodium nitrate is used as a fertilizer and for the preparation of nitric acid. (It is found in 'nitre beds' in Chile and Peru.)

Sodium thiosulphate is photographers' 'hypo'.

Potassium nitrate is used in making explosives and in preserving meat (saltpetre in bacon-curing).

Potassium permanganate is a useful disinfectant, and can be used for staining wood brown.

Ammonium chloride is used in dry cells and Leclanché cells.

Ammonium nitrate is used for making explosives.

Ammonium sulphate is used as a fertilizer.

EXAMPLES ON CHAPTER XXX.

1 Calculate the weight of sodium bicarbonate required to produce on heating 20 gm. of anhydrous sodium carbonate.

2 What weight of caustic soda will be required to liberate all the ammonia from 2 gm. of ammonium chloride? What volume of N . NaOH will be required for this purpose?

XXXI

CALCIUM, MAGNESIUM, AND ZINC

Experiment 103.

To find the Equivalent of Calcium.

Weigh out accurately in a small tube between 0·3 and 0·4 gm. of metallic calcium, previously cleaned by scraping with a file. Insert the tube into an inverted gas-jar full of water standing in a trough of water. Collect the hydrogen given off (the action may take some time to reach completion) and measure its volume. Remember the necessity for levelling the tube (see Chapter VI). Reduce the volume to N.T.P.

From the equation $Ca + 2H_2O = Ca(OH)_2 + H_2$, we see that the atomic weight of calcium would liberate 22·39 litres of hydrogen. Calculate the equivalent from the result of the above experiment, and show that calcium is divalent.

Metallic calcium somewhat resembles sodium in appearance. It is bright, but the surface is soon oxidized in air, although the action is much less rapid than with sodium. The metal does not have to be kept under mineral oil. The action on water is also, as we have seen, much less rapid. The metal is divalent in all its compounds, and, unlike sodium, has some almost insoluble salts, notably the sulphate and carbonate.

Calcium oxide, or quicklime, CaO, and calcium hydroxide, $Ca(OH)_2$, have already been discussed (Chapter VIII). We give here the equation for the formation of quicklime from limestone.

$$CaCO_3 \rightleftarrows CaO + CO_2.$$

This is another example of a reversible reaction. In a lime-kiln a good draught must be maintained to remove the carbon dioxide as it is formed, and thus prevent it from recombining with the quicklime. The slaking of lime is represented quantitatively as follows:

$CaO + H_2O = Ca(OH)_2$ (compare Experiment 29 (*b*)).

Slaked lime is the principal constituent of mortar. It is mixed with sand, which makes it porous and prevents it from crumbling when dry. As the mortar 'sets', the slaked lime combines both with the carbon dioxide of the air and with the silica (sand).

$$Ca(OH_2) + CO_2 = CaCO_3 + H_2O.$$
$$Ca(OH)_2 + SiO_2 = CaSiO_3 + H_2O.$$

These equations illustrate the similarity in chemical properties between the dioxides of carbon and silicon. It will be noted that water is given off in the process, thus explaining the dampness of newly-made walls.

The action of chlorine on the alkalies is most important.

(1) It reacts with cold, dilute caustic soda, caustic potash, or with lime-water, forming chlorides and hypochlorites thus:

$$Cl_2 + 2NaOH = NaCl + NaOCl + H_2O.$$
$$Cl_2 + 2KOH = KCl + KOCl + H_2O.$$
$$2Cl_2 + 2Ca(OH)_2 = CaCl_2 + Ca(OCl)_2 + 2H_2O.$$

The substances $NaOCl$, $KOCl$, $Ca(OCl)_2$ are the hypochlorites of sodium, potassium, and calcium respectively.

(2) It reacts with hot, strong caustic soda, caustic potash, or lime-water, forming chlorides and chlorates thus:

$$3Cl_2 + 6NaOH = 5NaCl + NaClO_3 + 3H_2O.$$
$$3Cl_2 + 6KOH = 5KCl + KClO_3 + 3H_2O.$$
$$6Cl_2 + 6Ca(OH)_2 = 5CaCl_2 + Ca(ClO_3)_2 + 6H_2O.$$

(3) It reacts with ammonium hydroxide, forming nitrogen

$$3Cl_2 + 8NH_4OH = 6NH_4Cl + N_2 + 8H_2O.$$

Unless ammonia is present in excess, dangerously explosive chlorides of nitrogen may be formed.

(4) It reacts with dry slaked lime, forming bleaching powder, as already mentioned in Chapter XV:

$$Ca(OH)_2 + Cl_2 = Ca(OCl)Cl + H_2O.$$

(5) It reacts with quicklime at a red heat liberating oxygen:

$$2CaO + 2Cl_2 = 2CaCl_2 + O_2.$$

The action of acids on bleaching powder is important.

(1) With weak acids, such as the carbonic acid of moist air, hypochlorous acid is formed, which decomposes in sunlight with liberation of oxygen. The nascent oxygen does the bleaching.

$$CaOClCl + H_2CO_3 = CaCO_3 + HCl + HOCl.$$

$$2HOCl = 2HCl + O_2.$$

(2) With strong acids chlorine is liberated:

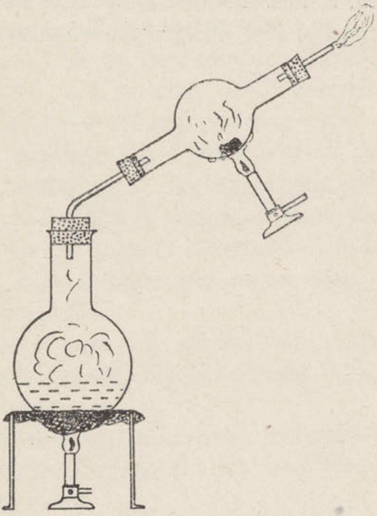
$$Ca(OCl)Cl + H_2SO_4 = CaSO_4 + Cl_2 + H_2O.$$

Of the other compounds of calcium we shall only mention here calcium chloride, $CaCl_2$, a useful laboratory drying agent, because it tends to form the hydrate, $CaCl_2 . 6H_2O$, and calcium sulphate, which in the form of plaster of Paris, $CaSO_4 . 2H_2O$, is used for making casts.

EXPERIMENT 104.

Action of Magnesium on Water.

Place a loose coil of magnesium ribbon in a bulbed tube, and connect the tube with a supply of steam at an angle which shall prevent condensed steam from reaching the bulb. Heat strongly, and when the magnesium is seen to react with the steam, light the issuing gas.



Magnesium oxide is left in the bulb, and the glass is attacked and usually falls to powder after this experiment. The equation for the reaction is:

$$Mg + H_2O = MgO + H_2.$$

Magnesium is a hard silvery metal, which is not tarnished by dry air, but slightly affected by moist air. It is very light and is also chemically active. It is one of the few elements which will combine directly with nitrogen, forming a nitride, Mg_3N_2. A certain amount of nitride is always formed in Experiment 47 (*a*), the burning of magnesium in air, and is one reason why this experiment does not give a satisfactory result. It is divalent in all its compounds. It burns with a very bright light forming the oxide, and is therefore used for photographic purposes.

$$2Mg + O_2 = 2MgO.$$

The oxide is only sparingly soluble in water, the solution having a feebly basic reaction. Magnesium metal is alloyed with aluminium to form magnalium. This alloy is stronger than aluminium and less easily corroded, and has therefore many uses.

EXPERIMENT 105.

Try to obtain hydrogen by the action of zinc dust on caustic potash solution.

$$Zn + 2KOH = K_2ZnO_2 + H_2.$$

Zinc is a hard silvery metal, tarnished by air to about the same extent as magnesium. It is not so light, nor so chemically active as magnesium. It burns in air or oxygen with a dazzling flame, forming the oxide:

$$2Zn + O_2 = 2ZnO.$$

This oxide is yellow when hot and white when cold. It is quite insoluble in water. The formation of potassium zincate, K_2ZnO_2, in which the zinc forms part of the acid radicle in Experiment 105, shows that zinc oxide can function as an acid oxide, for we can compare $K_2ZnO_2 = K_2O \cdot ZnO$ with say $K_2SO_4 = K_2O \cdot SO_3$. It is manufactured for use as white paint under the name of zinc white. Zinc is much used for galvanizing iron, the sheets of clean iron being dipped into molten zinc. As long as the zinc coating is not chipped away, the iron is protected from rust. The metal is also used for the poles of certain electric cells such as the Leclanché. Like calcium and magnesium, zinc is divalent in all its compounds.

The action of the acids on the three metals discussed in this chapter is considerably less violent than their action on sodium and potassium.

They dissolve in dilute or strong hydrochloric acid, liberating hydrogen from the acid and forming the chloride of the metal.

They dissolve in dilute sulphuric acid, liberating hydrogen from the acid and forming the sulphate of the metal.

They dissolve in hot strong sulphuric acid, reducing it to sulphur dioxide or sulphuretted hydrogen and forming the sulphate of the metal.

They dissolve in dilute or strong nitric acid liberating oxides of nitrogen from the acid and forming the nitrate of the metal.

(With very dilute nitric acid in the cold, magnesium alone of all metals liberates hydrogen.)

Equations representing these reactions will be given in the case of zinc and are similar for the other metals.

$Zn + 2HCl = ZnCl_2 + H_2$.

$Zn + H_2SO_4 = ZnSO_4 + H_2$ (dilute acid).

$Zn + 2H_2SO_4 = ZnSO_4 + SO_2 + 2H_2O$ (boiled with hot strong acid).

With nitric acid the products of the reaction vary very much with the concentration.

Principal Differences between Sodium and Calcium.

Sodium.	*Calcium.*
Monovalent.	Divalent.
Violent action on water.	Moderate action on water.
Oxide deliquescent.	Oxide not very soluble.
All salts soluble.	Some insoluble salts.

EXAMPLES ON CHAPTER XXXI.

1 What weight of calcium carbonate must be added to 1 litre of $5 \times N$ nitric acid in order to react as shown:

$$CaCO_3 + 2HNO_3 = Ca(NO_3)_2 + H_2O + CO_2.$$

2 Find the equivalent of magnesium from the following data: 2·5 gm. of the metal liberated 2·511 litres of hydrogen at 15° C. and 745 mm.

XXXII

COPPER. LEAD. IRON

The three metals which we shall discuss in this chapter each form more than one basic oxide, and consequently more than one set of salts. A table of these oxides is set out below.

All the oxides of these three metals are insoluble in water.

Copper.

Cuprous oxide Cu_2O, red-brown, basic oxide.
Cupric oxide CuO, black, basic oxide.

Lead.

Plumbic oxide, PbO, called massicot or litharge, yellowish-red, basic.
Red lead, Pb_3O_4, a mixed oxide, behaves with acids as a mixture of the two oxides PbO and PbO_2.
Lead peroxide, PbO_2, chocolate brown.
(There are also other less important oxides of lead.)

Iron.

Ferrous oxide, FeO, black, basic.
Magnetic oxide of iron, Fe_3O_4, black, a mixed oxide, behaves with acids as if it were a mixture of ferrous and ferric oxides.
Ferric oxide, Fe_2O_3, reddish-brown, basic.

EXPERIMENT 106.

Preparation of Cuprous Oxide and its action on Acids.

To some Fehling's solution add a solution of glucose. (Fehling's solution may be considered as an alkaline solution of cupric oxide.) Glucose is a reducing agent (see Experiment 31 (*c*)). Warm, and filter off and wash the bright orange or reddish precipitate of cuprous oxide. Divide the precipitate into two parts. To one add strong hydrochloric acid. The oxide dissolves, and on pouring into water a white precipitate of cuprous chloride is formed. To the precipitate add ammonia; the chloride dissolves and forms a deep-blue solution. (Cuprous chloride is soluble in hydrochloric acid and in ammonia, but insoluble in water.)

To the other add hot dilute sulphuric acid; a blue solution of copper sulphate (cupric, since cuprous is unstable) is formed, and copper is precipitated. The reactions may be represented as follows: $Cu_2O + 2HCl = Cu_2Cl_2 + H_2O$ and

$$Cu_2O + H_2SO_4 = CuSO_4 + H_2O + Cu.$$

Copper is a hard, reddish-brown metal, and is an excellent conductor of heat and electricity. It is much less brittle than zinc, being malleable (i. e. able to be beaten into foil) and ductile (able to be made into wire). It is slightly tarnished in moist air containing carbon dioxide. It does not act upon water. Dilute sulphuric acid and hydrochloric acid are without effect on it. With boiling strong sulphuric acid sulphur dioxide is produced as we have already seen (Experiment 51), and the metal is converted into sulphate.

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$

The metal readily dissolves in nitric acid, forming the nitrate and liberating oxides of nitrogen. Compare the behaviour of magnesium in Experiment 47 (*b*). The solution, when evaporated to dryness and ignited (see 'behaviour of nitrates on heating', Chapter XXV), yields cupric oxide.

Copper is used for electric cables and wires and for domestic utensils, and for many other purposes because of its inactivity. Alloyed with zinc, it forms brass.

Cupric oxide is insoluble in water, but soluble in acids forming cupric salts.

Cupric sulphate being poisonous, like all copper salts, is much used for spraying potatoes to keep off disease.

Cupric chloride is green, crystalline, and soluble, but

Cuprous chloride is white, amorphous, and insoluble in water, although soluble in strong hydrochloric acid and in ammonia. You will remember that copper ion gives a deep-blue colour with ammonia (Experiment 78).

EXPERIMENT 107.

Experiments on the Oxides of Lead.

(*a*) Heat some lead carbonate to low redness, thus converting it to lead oxide. $PbCO_3 = PbO + CO_2$.

(*b*) Try the action of dilute nitric acid on red lead. Filter, wash, and dry the product. Apply the usual tests to see if it is a peroxide. Red lead is a mixed oxide, and may be considered as $2PbO \cdot PbO_2$. When this is acted upon by nitric acid, the lead monoxide forms lead nitrate, and lead peroxide is precipitated.

(*c*) Heat some red lead very strongly in a hard glass tube, and test for oxygen. $Pb_3O_4 = 3Pb + 2O_2$.

If necessary repeat the heating of lead nitrate (Experiment 87) and the making of a lead bead on charcoal (Experiment 93).

Lead is a rather soft, very heavy silvery metal. It is very little attacked by air and moisture, and owing to this fact and to its softness it is much used for domestic water-pipes. The action of the acids on this metal corresponds to their action on copper, but the action with strong sulphuric acid is much slower owing to the great insolubility of lead sulphate which forms a layer on the surface of the metal and protects it from the action of the acid. In addition to its use for pipes, the metal is also used for making accumulator plates and in various alloys, such as pewter.

Lead Oxide is just soluble enough in water to make it alkaline to litmus.

White lead is basic lead carbonate. We discussed in Chapter XXI the meaning of an acid salt, and we have here an example of a basic salt, i. e. a salt retaining some of the hydroxyl of the base from which it is formed. It is much used for white paint.

EXPERIMENT 108.

To a cold solution of lead nitrate add dilute hydrochloric acid. A white precipitate of lead chloride is formed:

$$Pb(NO_3)_2 + 2HCl = PbCl_2 + 2HNO_3.$$

Boil, and the precipitate dissolves, but on cooling under the tap it reappears in crystalline form.

EXPERIMENT 109.

Experiments on the Oxides of Iron.

(1) Heat some ferrous oxalate (the ferrous salt of oxalic acid) in a test-tube until quite black. Shake out on to a tin tray. Note the incandescence, and that the black ferrous oxide produced in the tube is immediately oxidized by the air to red-brown ferric oxide.

$$4FeO + O_2 = 2Fe_2O_3.$$

(2) To a solution of ferric chloride add ammonia solution. Filter, wash, dry, and heat strongly the precipitate of ferric hydroxide, thus producing ferric oxide.

$$FeCl_3 + 3NH_4OH = Fe(OH)_3 + 3NH_4Cl.$$
$$2Fe(OH)_3 = Fe_2O_3 + 3H_2O.$$

(3) Repeat, if necessary, Experiment 18, in which steam is sent over red-hot iron. The black powder left in the tube is magnetic oxide of iron:

$$3Fe + 4H_2O \rightleftarrows Fe_3O_4 + 4H_2.$$

Note that this is a reversible reaction; if hydrogen is sent over red-hot magnetic oxide of iron, the oxide is reduced: if iron were heated with steam in a sealed tube we should get a balanced mixture of the four substances iron, hydrogen, water, and oxide of iron.

EXPERIMENT 110.

The different reactions of the Ferrous and Ferric Ions.

Make a solution of ferrous sulphate by picking out good green crystals, washing them with a little distilled water, and dissolving in cold, freshly-boiled distilled water. Note that the solution must not be heated, otherwise some of the ferrous sulphate will be oxidized by the air to ferric sulphate. Test this solution, and a solution of ferric chloride in the following ways:

(1) Add caustic soda solution, and note that ferrous hydroxide is white, but rapidly changes colour through dirty green to brown owing to oxidation by the air. Ferric hydroxide is red-brown.

(2) Add potassium ferricyanide solution, and note that it gives a dark blue precipitate (Prussian Blue) with a ferrous salt and a brown colour with ferric.

(3) Add potassium sulphocyanide solution, and note that it gives no colour with the ferrous salt, unless oxidation has taken place, and an intense dark red with ferric.

(4) Add potassium ferrocyanide solution and note the production of Prussian Blue with ferric chloride.

EXPERIMENT 111.

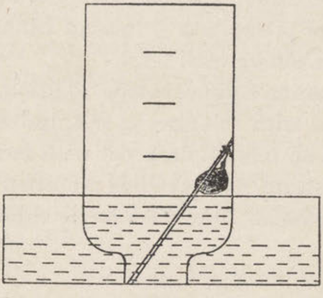
Rusting of Iron.

(*a*) *To show that both air and water are required for rusting.*

Boil some distilled water for twenty minutes, and when cold, pour it on to a clean iron nail in a test-tube. Cover the top of the water with oil. Place a similar clean nail half in and half out of some water in a second test-tube, and a third nail in another tube with a piece of quicklime. Leave for a week, and note that only the nail with both air and water and no lime (alkali) has become rusty.

(*b*) *To show that oxygen is taken up in rusting.*

Wrap some iron filings in a piece of muslin, and tie it to the end of a glass rod. Roughly divide a glass bottle (a caustic soda bottle is suitable) into five equal volumes by marking with black paint. Invert the bottle in water, and moisten the filings, and push them in on the rod. Leave for some days, and note that one-fifth of the air in the bottle (i. e. the oxygen) is used up. Test the remaining gas for nitrogen.



EXPERIMENT 112.

Heating Ferrous Sulphate.

Heat some ferrous sulphate crystals strongly in a hard glass tube. Lead the vapours given off into:

(*a*) potassium permanganate solution, which is decolorized by the sulphurous acid (reducing agent) produced.

(*b*) barium chloride solution, in which a precipitate of insoluble barium sulphate is formed by the sulphuric acid produced.

The brown residue in the tube is ferric oxide:

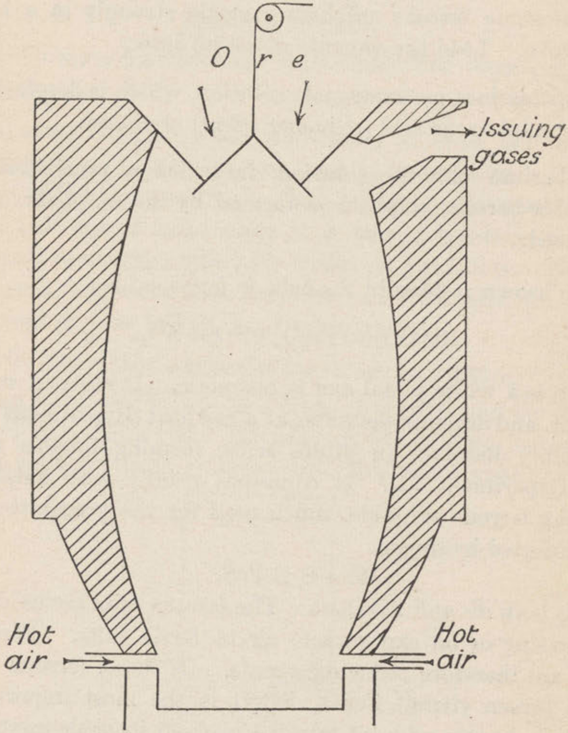
$$2FeSO_4 = Fe_2O_3 + SO_3 + SO_2.$$

Iron is a white metal and is magnetic. It rusts in water and air, and decomposes water at a red heat (Experiment 18). It readily dissolves in dilute acids, forming ferrous salts (see Experiment 71). It combines readily with sulphur, forming ferrous sulphide, much used for the preparation of sulphuretted hydrogen.

$$Fe + S = FeS.$$

It is both di- and trivalent. The ferrous salts are oxidized on heating or on exposure to air to ferric salts. Ferrous salts are therefore reducing agents. Of these, ferrous sulphate (green vitriol), $FeSO_4 . 7H_2O$, is the most important. When magnetic oxide of iron is dissolved in acids mixtures of ferrous and ferric salts are obtained. Ferric chloride is the most common ferric salt.

The principal ores of iron used for smelting are the oxide and the carbonate. These ores are first strongly heated in air to drive off water and carbon dioxide, burn up sulphur and other impurities, and make the ore porous. The ore is then mixed with coke and limestone, and shot into a blast-furnace. These furnaces have an elongated egg-shaped section as shown, and may be 50–100 ft. high.



A hot air-blast is blown in at the bottom, and the oxygen in it burns the coke: $C + O_2 = CO_2$.

The carbon dioxide is at once reduced to carbon monoxide:

$$CO_2 + C = 2CO.$$

The combustion of the coke raises the iron oxide to a high temperature, at which it is reduced by the carbon monoxide:

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2.$$

The iron produced melts (its melting-point is lowered by carbon which dissolves in it) and sinks to the bottom of the furnace, from which it is run off from time to time into moulds made in wet sand. The blocks of iron thus obtained are called 'pigs' and the iron 'pig-iron'.

Limestone is mixed with the iron ore in order that lime may be produced. The lime (CaO) unites with the silica (SiO_2) always contained in iron ores, and forms a glass (cf. Chapter XXIX) or 'slag'. This slag melts and sinks to the bottom of the furnace with the iron, but being less dense than liquid iron it floats on top of it and is run off separately.

The gases that issue from the top of the furnace contain enough carbon monoxide to make them combustible, and are used to heat the air-blast.

Pig-iron, or cast iron, contains a considerable proportion of carbon, and is very hard and brittle and crystalline. It is used for making stoves, cooking vessels, &c. A large amount of pig-iron is run, while still molten, into pear-shaped vessels, called Bessemer converters, where part of the carbon is burnt away by a blast of air, and the cast iron changed into steel.

Steel, which is much stronger than cast iron, is used for rails, tools, &c. Wrought iron, which contains no carbon, can also be obtained from cast iron by burning out all the carbon in a Bessemer converter, but steel is now used for most of the purposes for which wrought iron used to be prepared.

EXAMPLES ON CHAPTER XXXII.

1 The three oxides of iron contain 77·78, 70·00, and 72·41 per cent. of iron. Show that these numbers are in accordance with the Law of Multiple Proportions.

2 Find the formula of a substance which has the following percentage composition:

Na = 32·17 per cent.
Zn = 45·45 ,,
O = 22·38 ,,

ATOMIC WEIGHTS (APPROXIMATE)

Element.	*Symbol.*	*Atomic Weight.*	*Element.*	*Symbol.*	*Atomic Weight.*
Aluminium	Al	27	Lead	Pb	207
Antimony	Sb	120	Magnesium	Mg	24
Arsenic	As	75	Manganese	Mn	55
Barium	Ba	137	Mercury	Hg	201
Bismuth	Bi	208	Nickel	Ni	59
Bromine	Br	80	Nitrogen	N	14
Calcium	Ca	40	Oxygen	O	16
Carbon	C	12	Phosphorus	P	31
Chlorine	Cl	35·5	Platinum	Pt	195
Chromium	Cr	52	Potassium	K	39
Cobalt	Co	59	Silicon	Si	28
Copper	Cu	63·5	Silver	Ag	108
Fluorine	F	19	Sodium	Na	23
Gold	Au	197	Strontium	Sr	88
Helium	He	4	Sulphur	S	32
Hydrogen	H	1	Tin	Sn	119
Iodine	I	127	Zinc	Zn	65
Iron	Fe	56			

SATURATED VAPOUR PRESSURE OF WATER

Temp.	*Pressure.*	*Temp.*	*Pressure.*	*Temp.*	*Pressure.*
0° C.	4·6 mm.	11° C.	9·8 mm.	21° C.	18·6 mm.
1	4·9	12	10·5	22	19·8
2	5·3	13	11·2	23	21·0
3	5·7	14	12·0	24	22·3
4	6·1	15	12·8	25	23·7
5	6·5	16	13·6	26	25·1
6	7·0	17	14·5	27	26·7
7	7·5	18	15·5	28	28·3
8	8·0	19	16·5	29	29·9
9	8·6	20	17·5	30	31·7
10	9·2				

											Mean Differences.								
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6

											Mean Differences.								
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4
100	0000	0004	0009	0013	0017	0022	0026	0030	0035	0039									
101	0043	0048	0052	0056	0060	0065	0069	0073	0077	0082									
102	0086	0090	0095	0099	0103	0107	0111	0116	0120	0124									
103	0128	0133	0137	0141	0145	0149	0154	0158	0162	0166									
104	0170	0175	0179	0183	0187	0191	0195	0199	0204	0208									
105	0212	0216	0220	0224	0228	0233	0237	0241	0245	0249									
106	0253	0257	0261	0265	0269	0273	0278	0282	0286	0290									
107	0294	0298	0302	0306	0310	0314	0318	0322	0326	0330									
108	0334	0338	0342	0346	0350	0354	0358	0362	0366	0370									
109	0374	0378	0382	0386	0390	0394	0398	0402	0406	0410									
110	0414	0418	0422	0426	0430	0434	0438	0441	0445	0449									

	0	1	2	3	4	5	6	7	8	9	Mean Differences.								
											1	2	3	4	5	6	7	8	9
·00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
·01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
·02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
·03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
·04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
·05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
·06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
·07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
·08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
·09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
·10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
·11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
·12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
·13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
·14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
·15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
·16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
·17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
·18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
·19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
·20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
·21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
·22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
·23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
·24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
·25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
·26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
·27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
·28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
·29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
·30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
·31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
·32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
·33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
·34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
·35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
·36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
·37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
·38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
·39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
·40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
·41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
·42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
·43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
·44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
·45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
·46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
·47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
·48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
·49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6
·50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7

											Mean Differences.								
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
·50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
·51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
·52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
·53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
·54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
·55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
·56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
·57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
·58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
·59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
·60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
·61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
·62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
·63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
·64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
·65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
·66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
·67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
·68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
·69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
·70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
·71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
·72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
·73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
·74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
·75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
·76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
·77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
·78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
·79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
·80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
·81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
·82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
·83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
·84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
·85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
·86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
·87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
·88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
·89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
·90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
·91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
·92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
·93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
·94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
·95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
·96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
·97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
·98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
·99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

INDEX

Absolute temperature, 36.
Acetylene black, 176.
Acid salts, 131, 141.
— oxides, 46.
Acidimetry, 144 seq.
Acids, 46, 76, 109.
Air, 38, 224.
Alkali, 47, 77.
Alkalimetry, 144 seq.
Allotropy, 127, 174, 190.
Aluminium, 78, 204.
Ammonia, 153 seq., 194.
Ammonium, 155, 156.
— chloride, 13, 205, 206.
— hydroxide, 156, 205.
— nitrate, 164, 165, 205.
— sulphate, 153, 156, 160, 205.
Amorphous, 14.
Anhydrous, 14.
Animal charcoal, 176.
Anode, 29.
Antilogarithms, 232.
Aspirin, 179.
Atomic theory, 86.
Atomic weight, 87, 114.
Atomic weight table, 229.
Avogadro's Law, 33.

Baking powder, 59.
Barium chloride, 139, 161.
— peroxide, 118.
Base, 47.
Basic oxide, 46, 200.
— salt, 221.
Benzene, 163.
Berzelius, 88.
Bessemer converter, 227.
Black-lead, 175.
Blast furnace, 226.
Bleaching, 93, 136, 137.
— powder, 93, 212.
Boiling-point of water, 26.
Boyle's Law, 32, 36.
Breathing, 55, 56, 58, 120.
Bromine, 195, 196.
Bunsen burner, 185.

Calcium, 210-12, 217.
— bicarbonate, 67, 69.
— carbonate, 49, 52, 67, 71.
— chloride, 15.
— hydroxide, 49, 50, 210, 211, 212.
— oxide, 50, 51, 210, 212.
— sulphate, 6, 212.
Calculations, 36, 147, 198.
Calx, 39.
Carbon, Chapter XXVI, p. 174.
— dioxide, 52-67, 135, 136, 137, 182.
— disulphide, 7, 20, 127.
— monoxide, 180, 182.
Carbonates, Chapter X, p. 63, 204.
Cast iron, 227.
Catalytic action, 118, 119.
Caustic potash, 47, 203, 204, 205.
Caustic soda, 47, 48, 203, 204, 205.
Cavendish, 31.
Chalk, 50, 67.
Charcoal, 175, 176.
Charles's Law, 32.
Chemical change, 17, 18.
Chemical equivalent, Chapter XIII, p. 78.
Chemical properties of a gas, 62.
Chlorides, Chapter XVII, p. 101.
Chlorine, Chapter XV, p. 89, 195, 196.
Chlorine water, 93.
Chlorophyll, 58.
Cinnamon, 179.
Coal, 153, 175.
— gas, 178, 189.

Coco-nut charcoal, 176.
Compounds, Chapter IV, p. 19.
Conservation of mass, 18.
Constant proportions, 21.
Contact process, 139.
Copper, Chapter XXXII, p. 218.
— sulphate, 11, 14, 142.
Cotton, 163.
Crystallization, Chapter II, p. 11.

Dalton, 87, 88.
Davy lamp, 187.
Deliquescence, 202.
Density of gases, 116.
Diamond, 174.
Diffusion, 25, 33, 206.
Distillation, 69.
Double decomposition, 71, 73, 74, 75, 77.
Dulong and Petit, 117.

Electrolysis, 28, 107.
Element, 21.
Equations, 100.
Equivalent proportions, 83.
— weights, Chapter XIII, p. 78, 210.
Eudiometer, 31.

Faraday's Law, 108.
Fatty acids, 70, 71.
Fehling's solution, 219.
Ferric chloride, 101.
— ion, 223.
— oxide, 222.
Ferrous chloride, 96, 101.
— ion, 223.
— oxide, 222.
— sulphate, 142, 225.
— sulphide, 128, 129, 225.
Fertilizer, 172.
Filtrate, 6.
Fire extinguisher, 59.
Flame, Chapter XXVII, p. 184.
Flowers of sulphur, 127.
Formic acid, 180.
Freezing mixture, 58.

Gas carbon, 176.
Gay-Lussac's Law, 32.
Glass, 198.
Glucose, 56, 219.
Glycerin, 163.
Graham's Law, 206.
Graphite, 174.
Green vitriol, 225.
Guano, 152.
Gun-cotton, 163.

Haber's process, 153, 172.
Haemoglobin, 56.
Halogens, 195.
Hardness of water, Chapter XI, p. 68.
Holmes signal, 193.
Hydrates, 14.
Hydrocarbons, 182.
Hydrochloric acid, Chapter XVI, p. 94.
Hydrogen, Chapter V, p. 23, 124.

Ignition temperature, 184.
Indicators, 145.
Iodine, 196.
Ions, 108.
Iron, Chapter XXXII, p. 218.

Jet, 177.

Kathode, 28.
Kipp's apparatus, 53.

Lamp black, 176.
Lavoisier, 18, 39.
Lead, Chapter XXXII, p. 218.
Liebig condenser, 69.
Lime, 50.
Limestone, 50, 226.
Lime water, 50.
Liquids, 8.
Litharge, 218.
Litmus, 48, 145.
Logarithms, 230.
Lyddite, 179.

Magnesium, 16, 18, 78, 83, 213, 214.
Magnetic oxide of iron, 218, 222.
Manganese dioxide, 30, 118, 119.
Manures, 152, 153, 160.
Matches, 190.
Mercuric oxide, 40.
Metals, 200.
Methyl orange, 145.
Mixtures, 20, 21.
Molecular weight, 33, 34.

Molecule, 8, 9.
Mortar, 211.
Multiple proportions, 86, 87.

Natural waters, 71, 72.
Nitrates, 164.
Nitre, 5, 15.
Nitric acid, 161, 162, 163.
— oxide, 166, 168, 169, 170.
Nitrites, 169.
Nitro-benzene, 163.
Nitrogen, 38, 39, Chapter XXIV, p. 150, 172.
— dioxide, 167, 171.
— pentoxide, 167, 168, 171.
— trioxide, 166, 168, 171.
Nitro-glycerin, 163.
Nitrous acid, 169.
— oxide, 165, 168, 169, 170.
Non-metals, 200.
Normal solutions, 144.
— salts, 131.
Novocaine, 179.

Oxalic acid, 144, 145, 163, 180.
Oxidation, 121.
Oxides, Chapter VIII, p. 45, 121, 122.
Oxygen, Chapter VI, p. 30, 120.
Oxyhaemoglobin, 56.

Paraffin wax, 182.
Permanent hardness, 69.
Peroxides, 121.
Petrol, 182.
Petroleum, 182.
Phenol phthalein, 145.
Phosphine, 192, 194, 195.
Phosphoric acid, 162, 195.
Phosphorus, 41, 42, 43, Chapter XXVIII, p. 190.
— pentoxide, 191.
Physical change, 18.
Pig-iron, 227.
Plaster of Paris, 212.
Plastic sulphur, 127.
Plumbago, 175.
Potassium, 202.
— carbonate, 202.
— chlorate, 30, 35, 118, 119.
— hydroxide, 204.
— iodide, 123.
— nitrate, 5, 15, 118, 164, 208.
Potassium, permanganate, 118, 123, 208.
Priestley, 39.
Prismatic sulphur, 127.
Producer gas, 181.

Quartz, 197.
Quicklime, 50.

Rain water, 72.
Red lead, 218, 221.
Red phosphorus, 190, 191.
Reduction, 122, 123.
Refrigerator, 160.
Reversible reactions, 40, 129, 211.
Rhombic sulphur, 127.
River water, 72.
Rock salt, 105.
Rusting, 224.

Saccharin, 179.
Sal ammoniac, 15.
Saltpetre, 15.
Salts, 48, 74, 75, 76, 77, 110, 111, 112.
Sand, 197, 198.
Saturated solution, 4.
Sawdust, 163.
Silica, 197.
Silver nitrate, 105.
Slaked lime, 50, 211.
Soap, 70, 71.
Sodium, 201, 202.
— bicarbonate, 64, 65, 66, 67, 208.
— carbonate, 12, 64, 66, 67, 208.
— chloride, 104, 105, 208.
— hydroxide, 47, 48, 202, 203, 208.
— nitrate, 208.
— sulphate, 141.
— thiosulphate, 208.
Solids, 8.
Solubility, 5, 6.
Solution, Chapter I, p. 1.
Sparklets, 59.
Steel, 227.
Sublimation, 13.
Sugar, 140.
— charcoal, 176.
Sulphates, 142, 143.
Sulphur, 19, 126, 127, 128, 129.
— dioxide, 134, 135, 136, 137, 138.

Sulphur trioxide, 139.
Sulphuretted hydrogen, 129, 130, 131, 132, 133.
Sulphuric acid, 139, 140.
Sulphurous acid, 136.
Symbols, 88.

Table of atomic weights, 229.
— water vapour pressure, 229.
Temporary hardness, 69.
Titration, 146.

Valency, 101, 102.
Vapour density, 116.
Vine charcoal, 175, 176.
Vitriols, 143.
Voltameter, 28.

Water, 26, 27, 28, 29, 31, 68, 69, 71, 72.
Water-gas, 181.
Water of crystallization, 14.
White lead, 221.
Wood charcoal, 175.

Yeast, 59.

Zinc, 24, 78, 215, 216.

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